AD-A274 546

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
Unclassified	

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT
2b. DECLASSIFICATION/DOWNGRADING	APPROVED FOR PUBLIC RELEASE: DISTRIBUTION IS UNLIMITED

DTIC SELECTE JAN 11 1994 S B D

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
Rohm and Haas Company		

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
727 Norristown Road Spring House, PA 19477	

8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
Naval Research Laboratory		N00014-83-C-2339

94-01057

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
Washington, DC 20375	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK ACCESSION

11. TITLE (Include Security Classification)

Development of a Synthetic, Humidity Resistant, High Capacity Adsorbent for Collective Air Filters for Naval Vessels (Phase II)   210

12. PERSONAL AUTHOR(S)
Stephen, G. Maroldo, Louis A. Kaufell, Jr., Jeffrey L. McMurtrie

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Final	FROM 9/83 TO 8/85	1984 OCT 10	88

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	adsorbent, polymeric adsorbent, resin, filtration, humidity, air filtration, purification, pore distribution

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Synthetic polymeric adsorbents, which were characterized by BET surface area and mercury intrusion volume, were evaluated for their potential as adsorbent media for collective air purification filters. The equilibrium water isotherms were determined for the synthetic adsorbents and ASC Whetlerite. These adsorbents were then screened for their dynamic capacities to adsorb the organic vapors diisopropyl fluorophosphate (DFP), dimethyl methylphosphonate (DMMP), and 2-chloroethyl isobutyl sulfide (CIS) from flowing air streams. The most promising adsorbents were more thoroughly evaluated using the bed depth service time technique to determine the kinetic saturation capacities using DFP, DMMP, CIS, methylene chloride, toluene, and o-xylene which provided a correlation of kinetic saturation capacity with the volatility or normal boiling point of the adsorptive. The DFP testing was done under both dry and highly humid conditions. In all of the dynamic testing, ASC Whetlerite was used as a control adsorbent.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS	Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

DD Form 1473, JUN 86   Previous editions are obsolete.   SECURITY CLASSIFICATION OF THIS PAGE

94 1 10 035

**ROHM
!HAAS
COMPANY**

Development of a Synthetic, Humidity Resistant,
High Capacity Adsorbent for Collective Air
Filters for Naval Vessels (Phase II)

Stephen G. Maroldo; Louis A. Kaufell, Jr.; Jeffrey L. Mc Murtrie
Rohm and Haas Company
727 Norristown Road
Spring House, PA   19477

10 October 1984

Final Report for Contract Number
N-00014-83-C-2339

Prepared for
Naval Research Laboratory
Washington, DC   20375

93-30269

93 12 13 087

ACKNOWLEDGEMENT

DTIC QUALITY INSPECTED 5

Accession For		
NTIS GRA&I	☑	
DTIC TAB	☐	
Unannounced	☐	
Justification		
By		
Distribution/		
Availability Codes		
Dist	Avail and/or Special	
A-1		

ABSTRACT

Synthetic polymeric adsorbents, which were characterized by BET surface area and mercury intrusion volume, were evaluated for their potential as adsorbent media for collective air purification filters. The equilibrium water isotherms were determined for the synthetic adsorbents and ASC Whetlerite. These adsorbents were then screened for their dynamic capacities to adsorb the organic vapors diisopropyl fluorophosphate (DFP), dimethyl methylphosphonate (DMMP), and 2-chloroethyl isobutyl sulfide (CIS) from flowing air streams. The most promising adsorbents were more thoroughly evaluated using the bed depth service time technique to determine the kinetic saturation capacities using DFP, DMMP, CIS, methylene chloride, toluene, and o-xylene which provided a correlation of kinetic saturation capacity with the volatility or normal boiling point of the adsorptive. The DFP testing was done under both dry and highly humid conditions. In all of the dynamic testing, ASC Whetlerite was used as a control adsorbent.

TABLE OF CONTENTS

EXECUTIVE SUMMARY

This contract has completed the screening studies on the synthetic polymeric macroporous and macronet adsorbents. These screening studies consisted of dynamic capacity measurements with diisopropyl fluorophosphate (DFP), 2-chloroethyl isobutyl sulfide (CIS), and dimethyl methylphosphonate (DMMP) under dry conditions, and hardness determinations. The goal of the studies was to determine which samples warranted further and more detailed consideration in the program. The adsorbents with the lowest dynamic capacities and that were most susceptible to attrition were not considered for further studies.

Four polymeric macroporous adsorbents and one polymeric macronet adsorbent were studied further using the BDST technique. ASC Whetlerite was evaluated as a control for comparison. This technique measures breakthrough times as a function of bed height. In addition, a more varied series of challenges were used so that correlations could be developed with the volatility of the adsorbate. The adsorbents were challenged with methylene chloride, toluene, o-xylene, DMMP, DFP, and CIS under dry conditions. The synthetic adsorbents used in this study were not conditioned in any way prior to their evaluation. The ASC Whetlerite, however, was dried at 120°C and stored under vacuum prior to use.

Under conditions of low humidity, the BDST evaluation of the synthetic adsorbents and ASC Whetlerite showed a linear correlation with the boiling point of the adsorbent. The slope of the plot of kinetic saturation capacity vs boiling point of the adsorbate was greater for the synthetic adsorbents than it was for ASC Whetlerite. This indicates that the synthetic adsorbents have a lower kinetic saturation weight capacities for volatile adsorptives than ASC Whetlerite has, but higher kinetic saturation weight capacities for nonvolatile adsorptives such as DFP, CIS, and DMMP than ASC Whetlerite. Since the synthetic adsorbents have lower densities than ASC Whetlerite, the kinetic saturation volume capacities are comparable to that obtained with ASC Whetlerite under dry conditions.

The BDST technique was also used to evaluate adsorbents under conditions of high relative humidity with DFP. The synthetic adsorbents were conditioned for 24 hours under a 95% RH air stream prior to testing. The results show that when the conditioned adsorbents were challenged with a DFP stream at 95%, the adsorbents retained a large portion (up to 90%) of their dry kinetic saturation capacities.

ASC Whetlerite was also challenged with DFP under highly humid conditions. When the Whetlerite was conditioned under 95% RH for 24 hours prior to use, the BDST evaluation with DFP showed a loss of 90% of the kinetic saturation capacity of the carbon to adsorb the DFP from the challenge stream. However, further work showed that the ability of ASC Whetlerite to adsorb DFP was dependent on the method of the conditioning of the carbon.

LIST OF TABLES

LIST OF TABLES (Continued)

LIST OF FIGURES

LIST OF FIGURES (Continued)

I. **INTRODUCTION**

During the last few years, the Navy has become concerned with and made the decision that chemical weapons are a threat to the Navy (1). In order to protect a ship and its personnel against chemical attack, protective uniforms, gas masks, and an air purification system or collective air filtration system are required. The goal of the air purification system is to provide areas where the crew of the ship can work in a shirt sleeves environment without loss of efficiency and to provide areas where the crew can get rest and relaxation from the burdens of the chemically protective garment.

The heart of any collective air purification system is the adsorbent medium that is used to remove the toxic vapors from the air streams. The conventional adsorbent that is used in such systems is granular activated carbon(2) which appears to suffer degraded performance in highly humid environments where the Navy routinely operates(3,4). Granular activated carbon adsorbs water very strongly and if the air that is put through the filter is not pretreated or dehumidified, the carbon will be quickly saturated and rendered inefficient or useless.

Several papers describe the effect of moisture on the ability of granular activated carbon to remove common organic vapors from air streams. Jonas, Sansone, and Farris(5) evaluated the effect of moisture on the ability of granular activated carbon (NACAR G-352) as measured by the 1% breakthrough time. They found that the breakthrough times of dry carbon beds that were exposed to humid air streams containing chloroform vapors were independent of the humidity of the stream. However, when the carbon beds were preconditioned either statically or dynamically at the humidity of the challenge stream, the breakthrough times decreased rapidly as the relative humidity increased. This is in agreement with the results obtained by Nelson, Corrcia, and Harder(6)who studied activated carbon respirator performance with common organic solvent vapors such as isopropanol, acetone, carbon tetrachloride, benzene, hexane, 1-chlorobutane, and ethyl acetate. Portorzhinskii and Serpionova(7) investigated the effects of humidity on the removal of benzene vapors from air streams by granular activated carbon and found results that were consistent with the other studies cited.

The chemical defense literature has a number of reports describing the effects of moisture on the ability of granular activated carbon to pick up agent vapors from humid streams. Conlisk and Carr(8) reported that chloropicrin (PS) adsorption capacity of carbon beds that were preconditioned in a static humid atmosphere decreased with increasing relative humidity over the range of 32-80% RH. They also found that GB adsorption was independent of RH in the range of 15-80%. In a study in 1968,

Braman, Pritchard, and Wheeler(9) found that GB adsorption capacity on ASC Whetlerite was very sensitive towards humidity. They found that the GB capacity of the ASC Whetlerite dropped 40% and 65% as compared to dry capacity when run in 15% and 50% RH vapor streams respectively. In this study, Whetlerite samples were preconditioned dynamically. Stamperius and van Dongen(10) reported that GB adsorption on Norit impregnated 1mm charcoal that had been humidified in a dynamic air stream of 70% or 90% RH was independent of RH. However, results with dry Norit carbon in dry streams were not reported. Further work(11) with GA indicated that the adsorption capacity of -30+40 mesh BPL carbon was unaffected by 50% RH. However, at 85% RH, adsorption capacity of the BPL carbon for GA was reduced by 5%. The report states that the decrease in capacity of BPL carbon for GA may be as high as 25% in 100% RH streams. More recent work from the Defense Research Establishment Ottawa(12,13) indicates that humidity decreases the capacity of carbon to pick up carbon tetrachloride, bromobutane, 2-hexanol, and chloropicrin. The decrease in capacity is largest for the more volatile organic vapors. The effect of humidity is also dependent on whether the canister is dry or preequilibrated with moisture before running in a humid stream. The humid preconditioning followed by a humid challenge stream shows the highest loss of capacity.

The effects of humidity on carbon were also observed in investigations on the determination of the residual life of a charcoal filter using a vapor that is weakly adsorbed such as methane or ethane(14). In this test, a pulse of gas contained in an air stream is passed through a filter. The residual adsorption capacity of the carbon bed is proportional to the retention time of the pulse because only the adsorption sites that are not taken by heavy adsorbate molecules are available to the pulse gas. Medema and van Bokoven(15) as well as Bac, Sacco, and Hammarstron(16) reported that the retention time of a methane or ethane pulse that is passed through a carbon bed decreases with an increase in the relative humidity of the effluent air stream. These results imply that the adsorption sites of the carbon are taken up by water.

The adsorption of water vapor by granular activated carbon has been studied extensively by Dubinin and Serpinskii(17-21). The basic mechanism by which water vapor is adsorbed is the formation of hydrogen bonds between the oxygen atoms on the micropore wall surfaces of the carbon and the water molecules themselves. The adsorbed water molecules then become secondary adsorption centers through hydrogen bonds. Thus, the probability of adsorption of water increases at high partial pressures of water vapor. Since water molecules compete with organic vapor molecules for the active sites on the surface, moisture in a vapor stream has a significant influence on the capacity of an active carbon to remove the organic vapor from the air

stream(22-24). Once water has equilibrated on a sorbent surface, the rate of adsorption is displacement controlled rather than controlled by a competition for adsorption sites(25).

The above results suggest that granular activated carbon would be a less than ideal adsorbent filter medium for collective protection of Naval vessels from toxic agents where high humidity exposures would be encountered. A high capacity, hydrophobic adsorbent, which had less susceptibility to water adsorption and would maintain its capacity for toxic agents in highly humid environments would be much more suitable for an air filtration system for ships. It is the goal of this project to develop such an adsorbent.

Phase II of this program to develop new adsorbents for air filtration systems on Naval vessels has continued to screen synthetic adsorbents for their ability to remove toxic agents from flowing air streams. Four adsorbents, three macroporous adsorbents and one macronet adsorbent, was studied further using the BDST and the Jonas techniques to better assess their potential as adsorbents in both low and high humidity streams.

This report describes the application testing that was done on synthetic polymeric adsorbents to demonstrate their usefulness as adsorption media for air purification system. The data generated suggest that these adsorbents show promise for shipboard collective air purification devices and justify further investigation of these materials for this application.

II.   ADSORBENTS AND CHARACTERIZATION

The work discussed in this report utilize two types of adsorbents for screening and evaluation as sorbent medium in collective air filters aboard Naval vessels. These adsorbents are polymeric macroporous and polymeric macronet adsorbents. Both types of adsorbents are hydrophobic in nature which retain adsorption capacity for agent simulants under highly humid conditions. The methods of their preparation provides versatility in the choice of chemical structure, surface properties, and pore size distribution. The tailorability of these resins to a particular application has the potential of producing adsorbents with superior performance with respect to capacity, humidity resistance, attrition resistance, and regenerability when compared to conventional granular activated carbon.

The adsorbents described below were characterized using BET surface area and mercury porosimetry. The BET surface areas were obtained with a Quantasorb Surface Area Analyzer. The porosity data were obtained with a Micromeritics AutoPore 9200 mercury penetration porosimeter. All of the adsorbents discussed in this report were of a -16+20 mesh cut which was found to give identical pressure drop to that obtained with -12+30 mesh ASC Whetlerite(26).

A.   Polymeric Macroporous Adsorbents

Polymeric macroporous adsorbents are hard porous polymeric spheres with high surface areas(27). They are available in a variety of polarities and surface characteristics which permits a wide range of adsorption applications. Through synthetic variations, the pore size distribution, porosity, and surface area of an adsorbent can be optimized for a specific application.

The polymeric macroporous adsorbents used in this study were prepared by a suspension polymerization process that has been described in the literature (28-37). The process involves the use of an organic solvent (phase extender) in which the monomers are soluble and the polymers are insoluble. During the course of the polymerization, the polymer precipitates out of solution as a spherical particle which contains included phase extender. After the polymerization is complete, the phase extender is removed to give a spherical polymer particle with a continuous network of pores throughout.

The polymeric macroporous samples prepared under this program were characterized using BET surface area and mercury intrusion porosimetry. The data characterizing these adsorbents are summarized in Table I. This data is provided as a description of the adsorbents for reference when discussing the other data presented in this report.

B. Polymeric Macronet Adsorbents

The polymeric macronet adsorbents are hard porous polymeric spheres which have high surface areas and a narrow distribution of small pores. The adsorbents synthesized for this study were prepared by standard procedures described in the literature (38-45). The adsorbents that were synthesized under this contract were characterized by BET surface area and mercury porosimetry as shown in Table II. The inclusion of this data in this volume of this report is presented only as a description of the adsorbents.

TABLE I

CHARACTERISTICS OF POLYMERIC MACROPOROUS ADSORBENTS

Adsorbent	Adsorbent Preparation Number	BET Surface Area (m^2/g)	Mercury Intrusion Volume (cc/g)
P-1	EJL595	960	1.77
P-2	CH1220	881	1.94
	SGM767	964	1.64
	JLM4245	956	2.03
P-4	SGM777	924	1.18
P-5	SGM775	804	0.59
P-6	SGM747	806	1.50
P-7	SGM789	788	1.40
	SGM753	1201	1.55
P-8	SGM761	816	1.42
P-9	SGM783	992	2.13
P-10	JLM4219	996	1.45
P-11	JLM4287	822	1.62
P-12	JLM4227	816	-
P-13	JLM4285	755	1.04
P-16	JLM4221	532	0.80

TABLE II

CHARACTERISTICS OF POLYMERIC MACRONET ADSORBENTS

Adsorbent	Adsorbent Preparation Number	BET Surface Area (m^2/g)	Mercury Intrusion Volume (cc/g)
N-4	SGM787	878	0.42
N-5	SGM785	1270	0.67
N-7	SGM741	1020	0.97
N-8	CH1308	1320	0.90
	SGM911	1300	-
N-9	SGM907	996	-
	SGM1003	1440	-
N-10	SGM917	1050	-
N-11	SGM1005	1280	-
N-12	SGM919	706	-

III. WATER VAPOR ISOTHERMS

The affinity of an adsorbent medium for moisture can have a detrimental effect on the capacity of the adsorbent to remove organic vapors from air streams. Nelson, Corrcia, and Harder(6) have shown that moisture can decrease the ability of carbon to adsorb common organic vapors. More recently, Jonas, Sansone, and Farris (5) showed that humidified carbon showed reduced capacity to adsorb chloroform from flowing air streams. Since the Navy operates in high humidity environments, it is of interest to characterize the adsorbents prepared under this program for their ability to adsorb moisture.

The procedure(46) used to determine the water vapor adsorption isotherms consisted of placing tared weighing bottles containing approximately one gram of adsorbent over sulfuric acid solutions contained in sealed desiccators. The relative humidities (P/Po) of the atmosphere above the solutions are listed in Table III(47-49). The adsorbent samples were capped, removed, and weighed every three days until a constant weight was achieved. There was not a correlation between length of time of exposure of the sample to the moisture and the amount of water picked up or the relative humidity level.

The results obtained with the polymeric macroporous adsorbents and the polymeric macronet adsorbents are shown in Tables IV and V. respectively. The results are plotted as conventional isotherms in Figures 1 and 2 respectively. Each table and figure contains the data for the control run using BPL unimpregnated granular activated carbon.

The BPL results are in general agreement with those results obtained by Freeman and Reucroft (50). In both data sets, a sharp rise in the amount of water picked up begins at a P/Po value of approximately 0.4. This sharp rise continues throughout our isotherm up to P/Po value of 0.94 but begins to flatten out at P/Po values 0.8 or 0.9 in Reucroft's data. The deviation of our isotherm from Reucroft's at high P/Po values is probably due to condensation in our system since our measurements are made by less sophisticated technique.

Reucroft (50) reports the adsorption isotherm for ASC Whetlerite. He reports that ASC Whetlerite is more hydrophilic than unimpregnated BPL carbon below a P/Po of 0.7 but less hydrophilic above that P/Po value. The ionic impregnants apparently attack moisture at the low P/Po regions but then block capillary condensation by occupying and thus reducing the pore volume of the adsorbent.

The isotherms for both BPL carbon and ASC Whetlerite are Type V of Braunaur's classification (89), which corresponds to an isotherm which is concave towards the pressure axis and show significant capillary condensation. This type of isotherm (concave) typically indicates that the intermolecular forces are large compared to the forces of adsorption(53).

The isotherm shown in Figure 1 illustrates the hydrophobicity of the polymeric macroporous adsorbents relative to that of BPL granular activated carbon. With the exception of P-5 and P-9, the polymeric macroporous adsorbents pick up essentially no water. These two adsorbents show a low water vapor capacity in the region P/Po = 0.94. The polymeric macroporous adsorbent P-9 contains a small amount of a proprietary crosslinker which makes the surface slightly more hydrophilic. The polymeric macroporous adsorbent P-5 has a slightly lower water vapor capacity than P-9 but has a higher pickup than the other polymeric macroporous adsorbents prepared from styrene-divinylbenzene. The reason for this is not readily apparent. The P-5 adsorbent has a lower degree of phase extension and thus a lower mercury intrusion volume than the P-9 sample.

The polymeric macronet adsorbents show a greater variation of water vapor adsorption at high relative humidities. With the exception of N-7, there is more variation of the amount of water picked up by the macronet samples than with the polymeric macroporous adsorbents. The samples range from being equivalent to ASC Whetlerite in water pickup to essentially no water pickup. Since the macronet adsorbents should be as hydrophobic as the macroporous adsorbents, the reason for the observed behavior is not known at this time. However, except for N-12, significant water pickup is not seen until the higher values of P/Po and then it is rather dramatic. One can not rule out the possibility of condensation which would render the values higher than expected.

Our BPL carbon data were also plotted according to the Dubinin-Polanyi equation (51-55):

$$\log W = \log Wo - ke^2 \tag{1}$$

where

$$e = RT\ln(Po/P)^2 \tag{2}$$

$$k = B/(2.303)^3 R^2 \tag{3}$$

In these equations W is the volume of condensed adsorbate, P is the equilibrium pressure of adsorbate vapor, Po is the saturated vapor pressure of liquid at temperature T K and Wo and B are constants related to the pore structure of the adsorbent. The ratio P/Po is the relative humidity of the atmosphere above the sulfuric acid solutions. Determination of the value of k could lead to the calculation of an experimental affinity coefficient (53-55).

TABLE III

SULFURIC ACID SOLUTIONS USED TO GENERATE
CONSTANT RELATIVE HUMIDITY FOR WATER STATIC ADSORPTION CAPACITIES

$[H_2SO_4]$ (%)[†]	Density of Acid Solution* (g/mL)	Relative Humidity (RH)
78.0	1.70	3.2
60.0	1.50	18.8
50.0	1.40	37.1
40.0	1.30	58.3
34.0	1.25	70.4
28.0	1.20	80.5
15.0	1.10	93.9

*Weast, R. C., ed "Handbook of Chemistry and Physics," 54th Edition, 1973, p. E-46.

[†]Weast, R. C., ed "Handbook of Chemistry and Physics," 54th Edition, 1973, p. D-230.

TABLE IV

STATIC WATER CAPACITY FOR POLYMERIC
MACROPOROUS ADSORBENTS AS A FUNCTION OF RELATIVE HUMIDITY

Adsorbent/RH (%)	Capacity (mg/g)						
	3.2	18.8	37.1	58.0	70.4	80.5	93.9
BPL Carbon	7.8	8.4	19.4	183	327	399	496
P-1 (EJL595)	5.0	0.0	0.8	0.2	3.0	4.8	7.6
P-2 (CH1220)	4.6	4.0	0.7	4.0	3.9	4.3	3.2
P-2 (SGM767)	3.7	0.0	0.0	2.6	2.0	1.4	3.8
P-4 (SGM777)	4.8	4.0	0.6	0.0	0.6	5.0	4.8
P-5 (SGM775)	4.8	0.0	0.0	1.2	0.8	2.3	20.8
P-9 (SGM783)	4.8	0.0	0.0	5.2	7.8	8.5	34.6
P-17 (SGM789)	1.4	0.0	0.0	2.9	0.0	0.2	5.8

TABLE V

STATIC WATER CAPACITY FOR POLYMERIC
MACRONET ADSORBENTS AS A FUNCTION OF RELATIVE HUMIDITY

Adsorbent/RH (%)	Capacity (mg/g)						
	3.2	18.8	37.1	58.0	70.4	80.5	93.9
BPL Carbon	7.8	8.4	19.4	183	327	399	496
N-4 (SGM787)	0.0	0.0	2.2	2.0	0.8	3.3	13.0
N-5 (SGM785)	0.0	0.0	1.6	5.6	8.6	13.3	249
N-7 (SGM741)	0.0	0.0	0.4	1.2	0.2	2.8	3.4
N-8 (SGM911)	1.4	1.6	2.5*	5.7	5.0	6.6*	231
N-10 (SGM917)	1.1	2.1	1.5	8.5	10.9	19.0	515
N-12 (SGM919)	1.3	8.1	6.3	24.4	41.6	50.8	305

---

*N-8 sample used was preparation JLM4515.

WATER ISOTHERM FOR MACROPOROUS ADSORBENTS
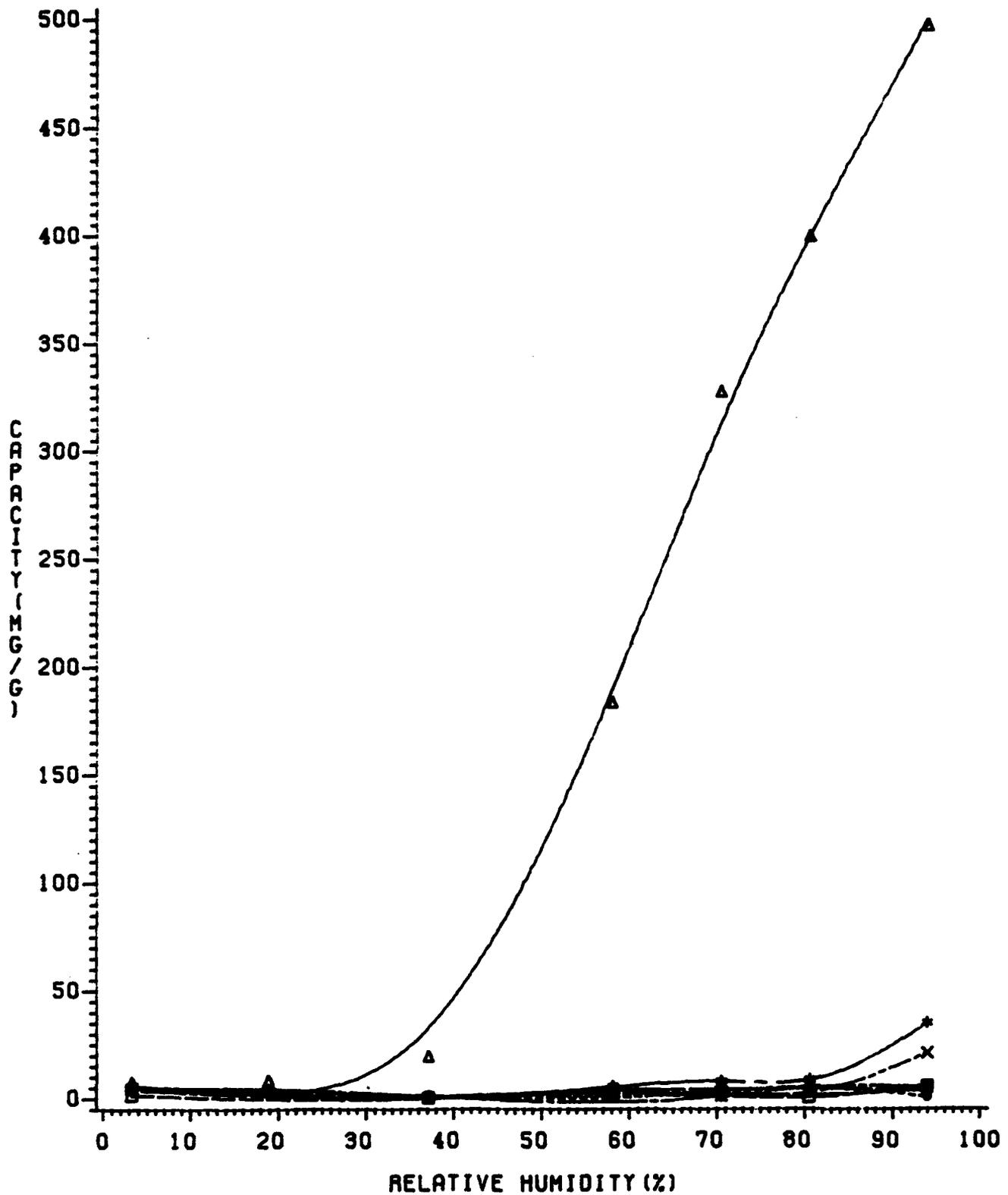
LEGEND: BED   △—△—△ BPL   ◆--◆--◆ P-1   ⊟—⊟—⊟ P-17   ◆—◆—◆ P-2
          +—+—+ P-2'   ◆—◆—◆ P-4   ✕—✕—✕ P-5   +—+—+ P-9

WATER ISOTHERM FOR MACRONET ADSORBENTS
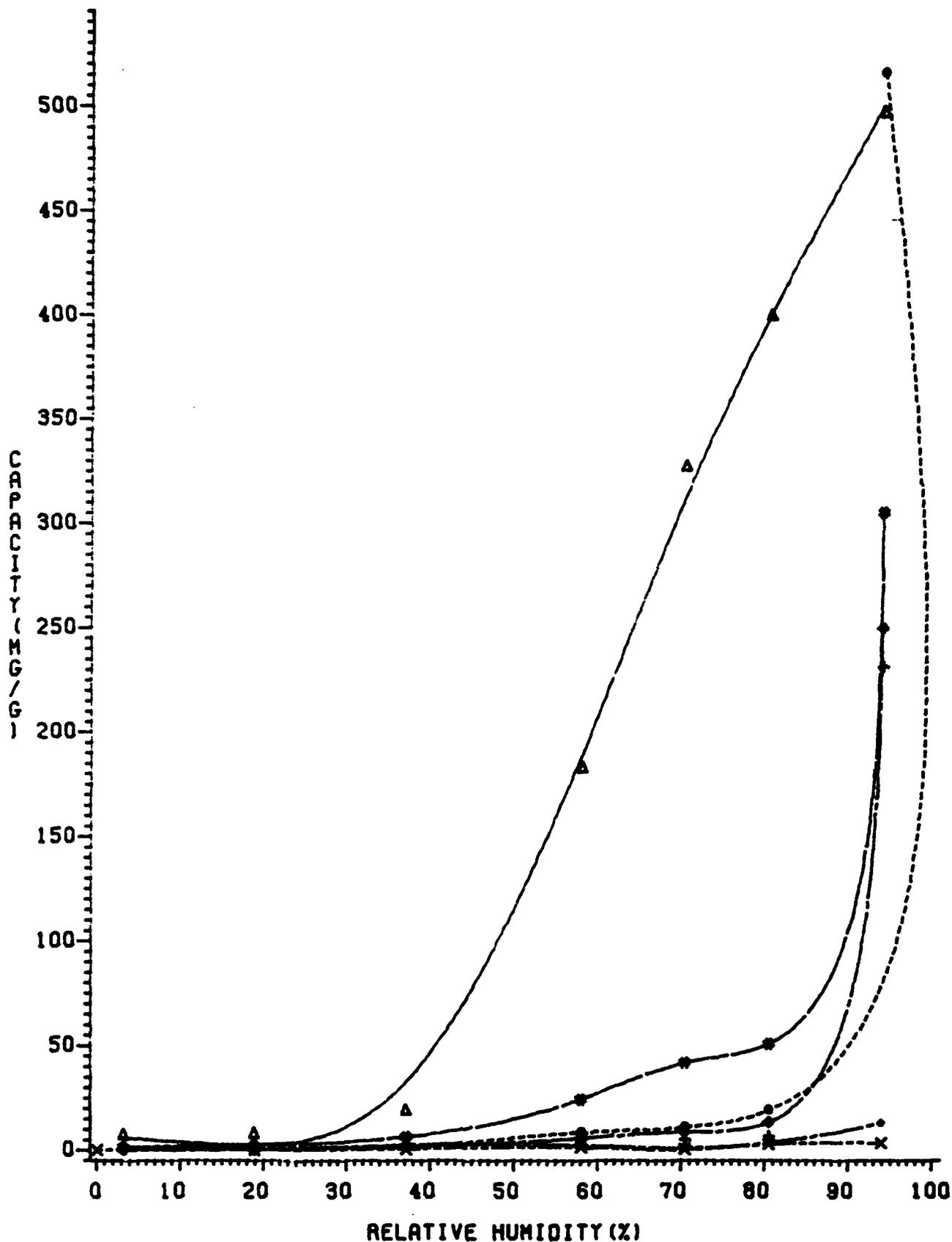
The BPL carbon data in the Dubinin-Polanyi form are summarized in Table VI and plotted in Figure 3. In agreement with Reucroft's (50) results, it can be seen from Figure 3 that the Dubinin-Polanyi plot is non-linear so k can not be evaluated.

The Dubinin-Polanyi treatments for the polymeric macronet adsorbents are summarized in Table VII. As can be seen from the correlation coefficients listed in the Table, this treatment did not produce a linear isotherm so that k can not be evaluated. The treatment The macronet Dubinin-Polanyi plot is shown in Figure 4. was not attempted on the data derived from the macroporous adsorbents since the water pickup was so low.

TABLE VI

BPL GRANULAR ACTIVATED CARBON WATER VAPOR
ADSORPTION ISOTHERM DATA IN THE DUBININ-POLANYI FORM

P/P_O	RT $\ln(P_O/P)$ [*]	E^2 [**] $\times 10^{-6}$	W	log W
0.032	2011	4.04	0.0078	-2.11
0.188	876	0.953	0.0084	-2.08
0.371	579	0.335	0.0194	-1.71
0.580	318	0.101	0.183	-0.738
0.704	205	0.0420	0.327	-0.485
0.805	127	0.0161	0.379	-0.399
0.939	36.8	0.00135	0.496	-0.305

[*] T = 294 K

[**] $E^2 = [RT \ln (Po/P)]^2$

FIGURE 3.

DUBININ-POLANYI PLOT OF WATER ISOTHERM

EPSILON SQUARED X10**-6

LEGEND: BED
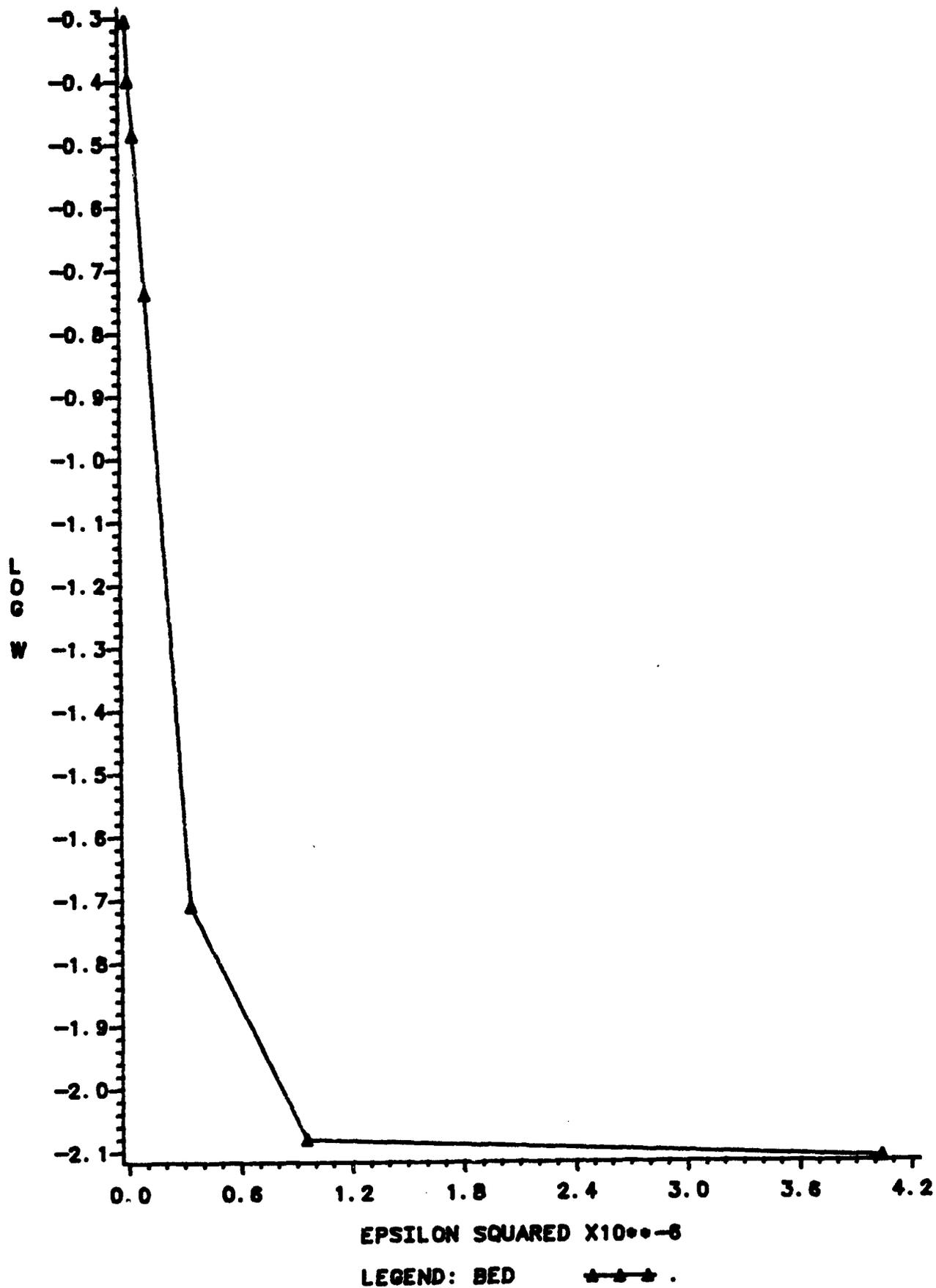
TABLE VII

POLYMERIC MACRONET WATER VAPOR ADSORPTION
ISOTHERM DATA IN THE DUBININ-POLANYI FORM

$E^2 \times 10^{-6}$*	N-4	N-5	log W			
			N-7	N-8	N-10	N-12
4.04	-	-	-	-2.85	-2.96	-2.89
0.953	-	-	-	-2.80	-2.68	-2.09
0.335	-2.66	-2.80	-3.40	-2.60	-2.82	-2.20
0.101	-2.70	-2.25	-2.92	-2.24	-2.07	-1.61
0.0420	-3.10	-2.07	-3.70	-2.30	-1.96	-1.38
0.0161	-2.48	-1.88	-2.55	-2.18	-1.72	-1.29
0.00135	-1.89	-0.604	-2.47	-0.636	-0.288	-0.516

Intercept:	-2.48	-1.48	-2.82	-2.04	-1.81	-1.40
Slope :	-8.65×10^{-7}	-4.40×10^{-6}	-1.90×10^{-6}	-2.43×10^{-7}	-3.38×10^{-7}	-4.03×10
r :	-0.2694	-0.7436	-0.4894	-0.4772	-0.5438	-0.7780

* $E^2 = RT \ln(P/PO)$

DUBININ–POLANYI PLOT OF WATER ISOTHERMS
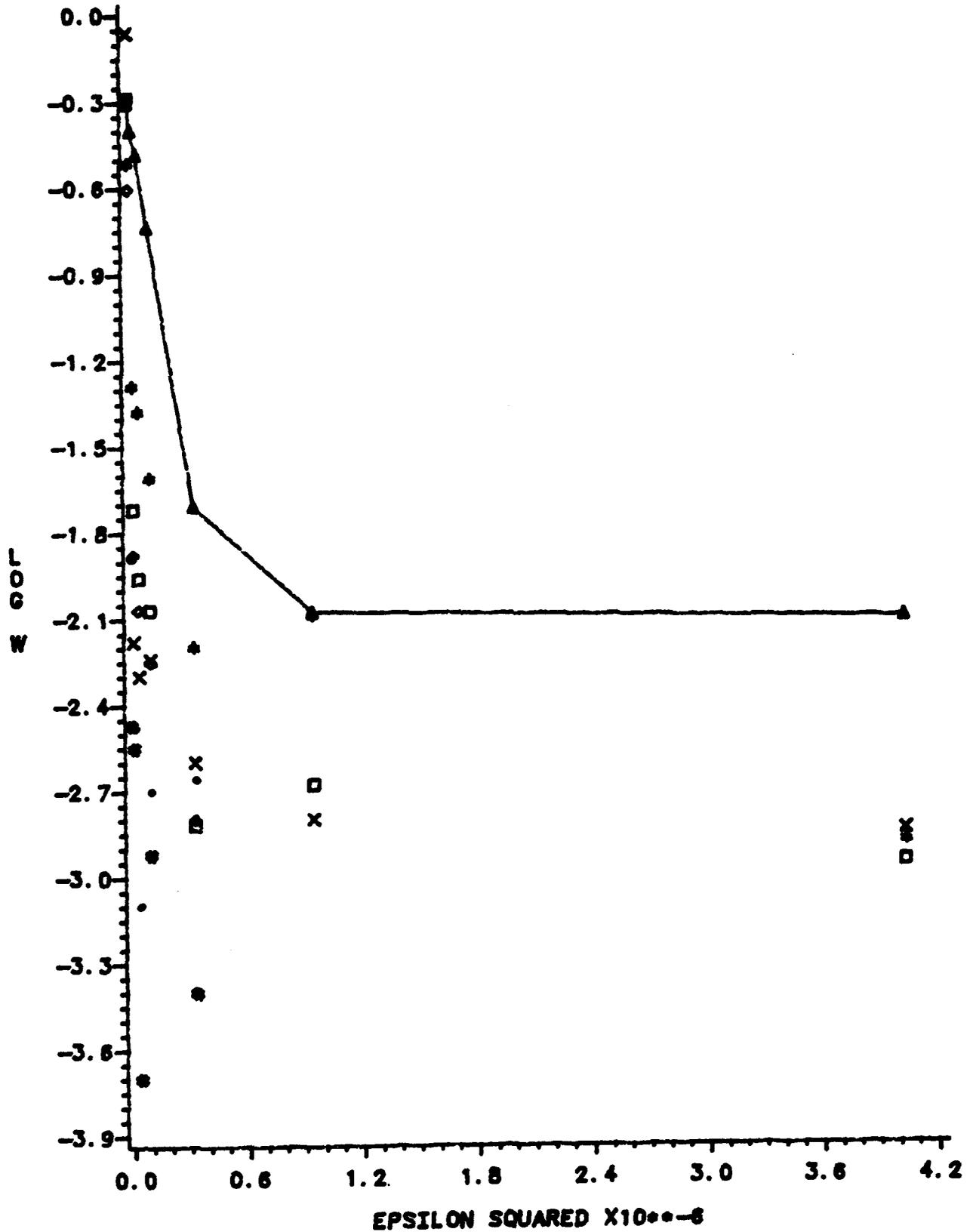
LEGEND: BED   ▲▲▲ ASC   □ □ □ N–10   ✦ ✦ ✦ N–12   • • • N–4
                 ◇ ◇ ◇ N–5   ⬢ ⬢ ⬢ N–7   × × × N–8

IV. DYNAMIC ADSORPTION TESTING

A. Apparatus

The dynamic testing apparatus at Rohm and Haas is diagrammed in Figure 2. It generates vapor streams by passing air over the surface of liquid adsorbated contained in a bubbler. This stream can then be calibrated gravimetrically using a large carbon cartridge before and after a run. The influent stream can be run dry or humidified. The relative humidity of the stream is calibrated using a Humicap 14 humidity indicator.[69] The challenge stream is then passed into a fixed bed of adsorbent and the effluent monitored with a Hewlett-Packard 5880 gas chromatograph equipped with a flame ionization detector, nitrogen-phosphorus detector, or electron capture detector. Data reduction of test runs is accomplished by an onboard micro processor interfaced with two GC terminal recorders. These provide continuous monitoring of tests in a convenient strip chart. Each chromatogram of test effluent is plotted and pertinent data (e.g. retention time, peak height, peak area and total area) are automatically calculated and printed.

The dynamic adsorption apparatus provides two completely independent gas challenge streams. Zero grade air is passed through a drierite trap to remove any trace levels of water vapor that may be present. This stream is split to provide feed to each simulant bubbler and Mulligan jar for humidification if needed. Once the desired run conditions have been set, the streams pass through rotometers and needle valves for precise flow regulation to the vapor generator. The metered simulant vapor then enters a mixing chamber (1 liter, 3 neck flask) after which it is passed through the adsorbent bed.

Testing of adsorbent is performed in a 1 cm wide, 20 cm high glass column fitted with a sintered disc of suitable porosity fixed at its mid-point. Typically a 1 gm sample was used except in bed depth studies where 1 to 3 inches of material were used. Flow rates were routinely set a 1 L/min. A portion of the effluent from the above column enters the GC for analysis with the remainder scrubbed through a bubbler containing 4% caustic and vented to the hood. All tubing and fittings are either stainless steel (316) or teflon.

The concentration of the challenge stream is calibrated gravimetrically using a large carbon cartridge at the start and finish of a run.

In the case of DFP humid streams, calibration is accomplished by using fluoride ion electrode to determine fluoride concentrations of a caustic solution contained in an impinger.
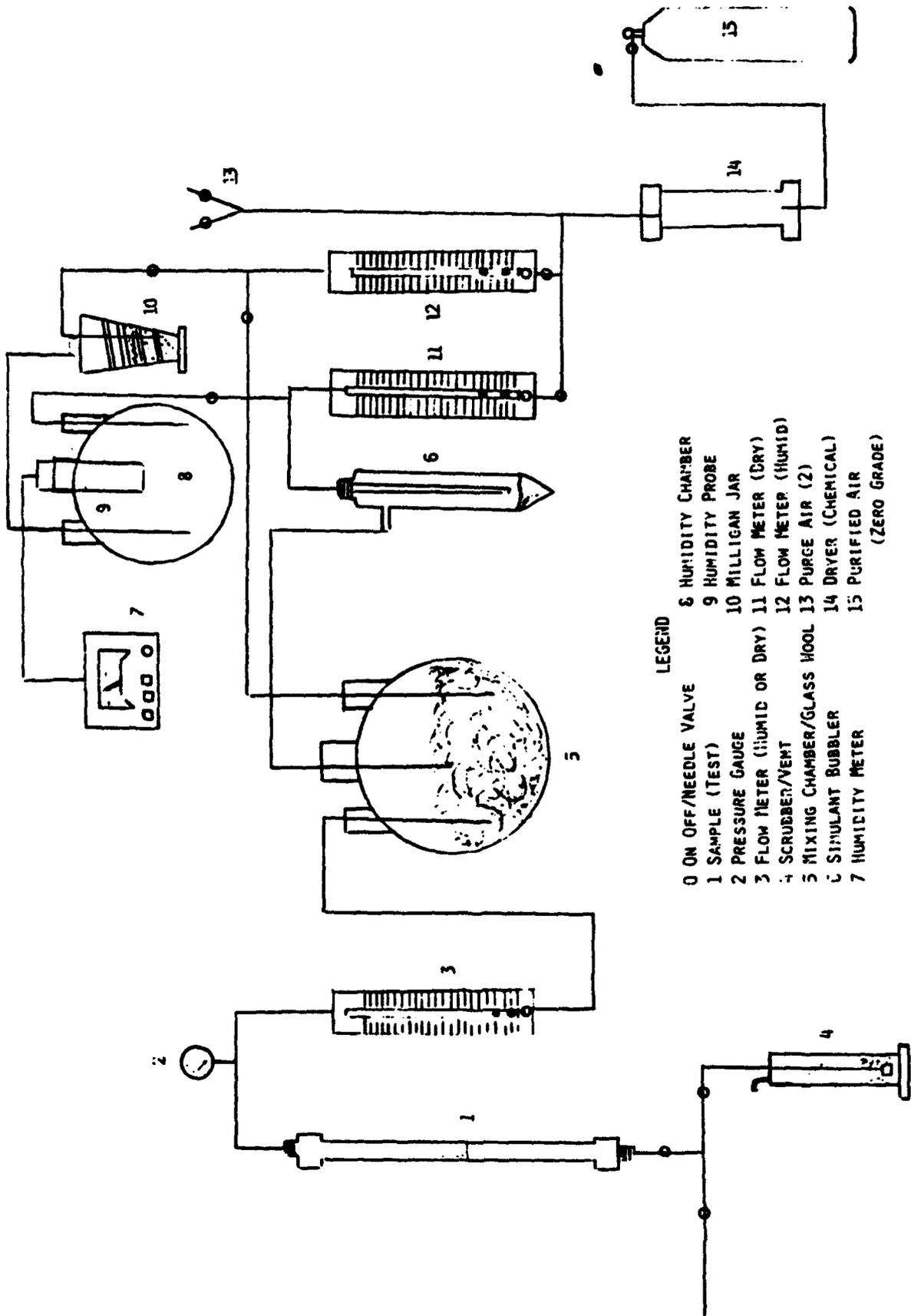
LEGEND

0 ON OFF/NEEDLE VALVE   8 HUMIDITY CHAMBER
1 SAMPLE (TEST)   9 HUMIDITY PROBE
2 PRESSURE GAUGE   10 MILLIGAN JAR
3 FLOW METER (HUMID OR DRY) 11 FLOW METER (DRY)
4 SCRUBBER/VENT   12 FLOW METER (HUMID)
5 MIXING CHAMBER/GLASS WOOL 13 PURGE AIR (2)
6 SIMULANT BUBBLER   14 DRYER (CHEMICAL)
7 HUMIDITY METER   15 PURIFIED AIR
                           (ZERO GRADE)

FIG. 5 SCHEMATIC DIAGRAM OF VAPOR CHALLENGE APPARATUS

Breakthrough for DMMP and DFP was an area count of 1000 to 1200 counts above background which corresponds to a concentration of approximately 1 g/L. Breakthrough for CIS was taken at 25 to 100 counts above background which corresponds to a concentration of approximately 10 g/L.

B. Screening Studies

During the course of this project, a large number of synthetic adsorbent samples were prepared which varied surface area, and porosity. The large number of samples prohibited the thorough investigation of each sample, so a screening program was utilized in Phase I (26) and continued in Phase II. This program consisted of measuring the lifetime of a one gram sample when challenged with vapor streams containing the simulants diisopropyl fluorophosphate (DFP), dimethyl methylphosphonate (DMMP), and 2-chloroethyl isobutyl sulfide (CIS). These challenges were done at very low humidity and compared to the results obtained with ASC Whetlerite under identical conditions. The synthetic samples with the greatest lifetimes were then considered for further testing which consisted of screening at very high (95%) relative humidity.

1. Low Humidity Screening Studies.

The results of the DFP screening studies that were obtained with the polymeric macroporous adsorbents are tabulated in Table VIII and plotted against challenge concentration in Figure 6. The results indicate that there is a trend towards higher capacity as the challenge concentration increases. This appears to occur independent of the polymeric adsorbent formulation and does not allow differentiation of the different samples. However, P-13 and P-16 were only challenged at the low concentrations and since these adsorbents had the lowest mercury intrusion volume and surface area, it may be not be appropriate to extend the trend to these adsorbents. The reason that the three values for P-2 (lot SGM767) fall off of the general correlation is not known.

The results of the DFP macronet screening studies are tabulated in Table IX and shown plotted against concentration in Figure 7. It is immediately evident from Figure 7 that there is not a clear dependence of capacity on the concentration of the challenge stream. It is also evident that the scatter in the data is more severe in the case of the macronets than with the macroporous adsorbents. It must be remembered that the synthetic

adsorbents are not preconditioned in any way prior to testing which probably enhances the scatter in the experimental results. due to differences in the water pickup of the different samples as was shown on the water equilibrium isotherms in Figure 2. However, the macronets N-8 and N-11 may be giving indications of a trend toward increasing capacity with increasing challenge concentration. In order to accept this hypothesis for the N-8 sample, however, the capacity obtained at a challenge concentration of 2.49 mg/L must be in error on the low side.

Table X summarizes the DMMP screening results obtained with the synthetic polymeric macroporous adsorbents and macronet adsorbents. These dynamic capacity are in addition to the values that were obtained and previously reported(26). The results are plotted against the challenge concentration in Figure 8. As can be seen from Figure 8, the dynamic DMMP capacities have considerably more scatter than the analogous DFP plot (Figure 7). However, there appears to be three groups or

TABLE VIII

RESULTS OF THE SCREENING STUDIES WITH DFP
OF THE POLYMERIC MACROPOROUS ADSORBENTS
UNDER LOW HUMIDITY

Adsorbent (Lot)	BET Surface Area m^2/g	Hg Intrusion Volume (cc/g)	Challenge Concentration (mg/L)	Breakthrough Time (min)	Capacity (mg/g)
P-1(EJL-595)	960	1.77	0.80	372	291
			2.37	183	424
P-2(SGM767)	964	1.64	0.75	340	251
(SGM767)	964	1.64	0.88	414	362
(JLM4245)	956	2.03	1.98	208	410
(CH1220)	881	1.94	2.12	162	343
(SGM767)	964	1.64	2.51	170	418
(SGM767)	964	1.64	2.56	216	530
(JLM4245)	956	2.03	2.92	145	448
P-10(JLM4219)	996	1.45	2.35	143	334
			2.45	162	384
P-11(JLM4287)	822	1.62	2.45	145	352
P-12(JLM4227)	816	-	1.90	220	394
			2.06	211	421
P-13(JLM4285)	755	1.07	2.05	107	204
			2.20	141	307
P-16(JLM4221)	532	0.80	1.60	102	156

FIGURE 6.

DYNAMIC DFP CAPACITY OF MACROPOROUS ADSORBENTS
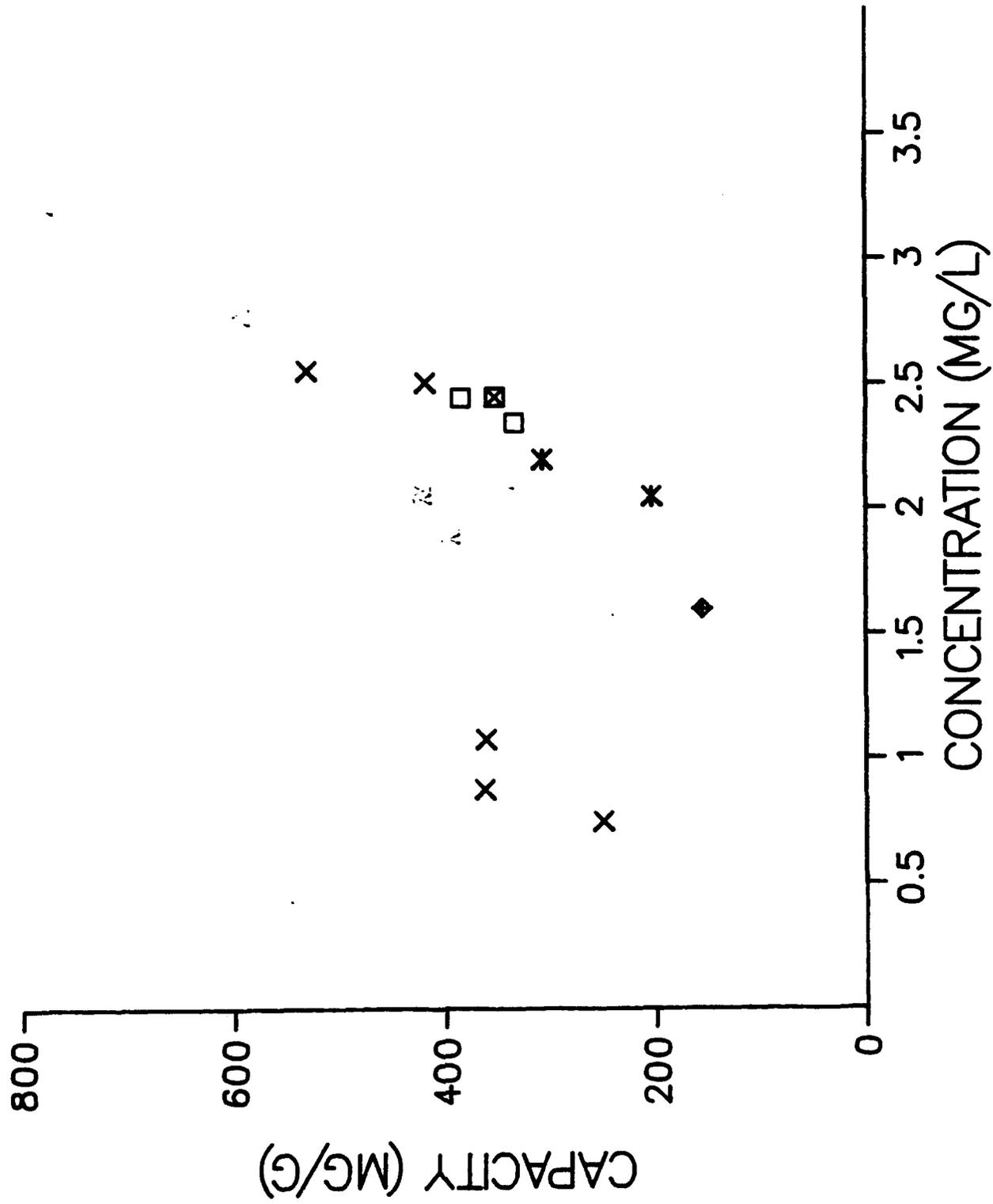
Legend
- △ P-2(CH1220)
- ✕ P-2(SGM767)
- □ P-10
- ▣ P-11
- ☒ P-12
- ✳ P-13
- ◆ P-16

CAPACITY (MG/G)

CONCENTRATION (MG/L)

TABLE IX

RESULTS OF THE SCREENING STUDIES WITH DPP
ON THE POLYMERIC MACRONET ADSORBENTS
UNDER LOW HUMIDITY

Adsorbent (Lot)	BET Surface Area (m^2/g)	Challenge Concentration (mg/L)	Breakthrough Time (min)	Capacity (mg/g)
N-8(SGM911)	1300	1.75	305	497
		1.85	590	643
		2.39	483	1100
		2.49	288	682
N-9(SGM1003)	1440	2.55	174	443
(SGM907)	996	2.38	172	404
N-10(SGM917)	1050	2.43	187	453
		2.44	130	299
		2.94	81	238
N-11(SGM1005)	1280	2.19	180	381
		2.58	357	406
		2.58	303	706
N-12(SGM919)	706	2.91	6	17

FIGURE 7.

DYNAMIC DFP CAPACITY OF MACRONET ADSORBENTS

Legend
- △ N-8
- × N-9
- □ N-10
- ▣ N-11
- ぷ N-12

CAPACITY (MG/G)
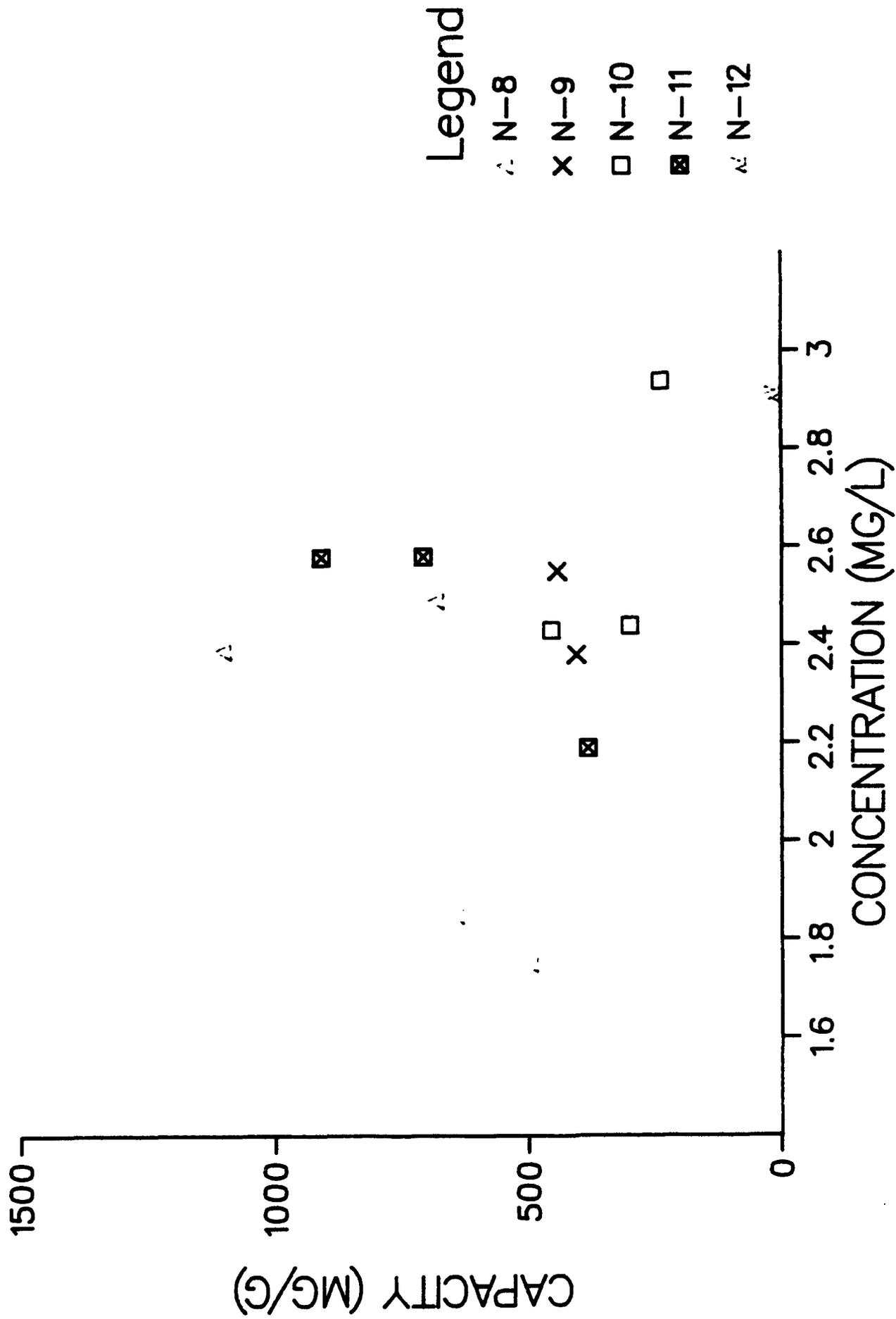
CONCENTRATION (MG/L)

TABLE X

RESULTS OF THE SCREENING STUDIES WITH DMMP OF THE POLYMERIC ADSORBENTS UNDER LOW HUMIDITY

Adsorbent	BET Surface Area (m^2/g)	Hg Intrusion Volume (cc/g)	Challenge Concentration (mg/L)	Breakthrough Time (min)	Breakthrough Capacity (mg/g)
P-1	960	1.77	2.23	57	170
P-2 (CH1220)	881	1.94	1.85	137	1252
(CH1220)			2.16	130	277
(JLM4245)	956	2.03	2.32	128	282
P-4	924	1.18	2.22	52	115
			2.33	48	108
P-5	804	0.59	2.26	51	113
			2.20	37	81
P-6	806	1.50	2.50	179	457
P-7	1201	1.55	2.37	195	459
P-8	816	1.42	2.22	116	257
P-10	996	1.45	2.11	236	494
			2.19	116	255
P-11	822	1.62	2.24	119	238
P-12	816	-	1.78	72	126
			1.81	117	210
P-16	532	0.80	2.14	39	83
N-9	1440	-	2.20	223	472
N-12	706	-	2.62	183	441

FIGURE 8.

DYNAMIC DMMP CAPACITY OF POLYMERIC ADSORBENTS
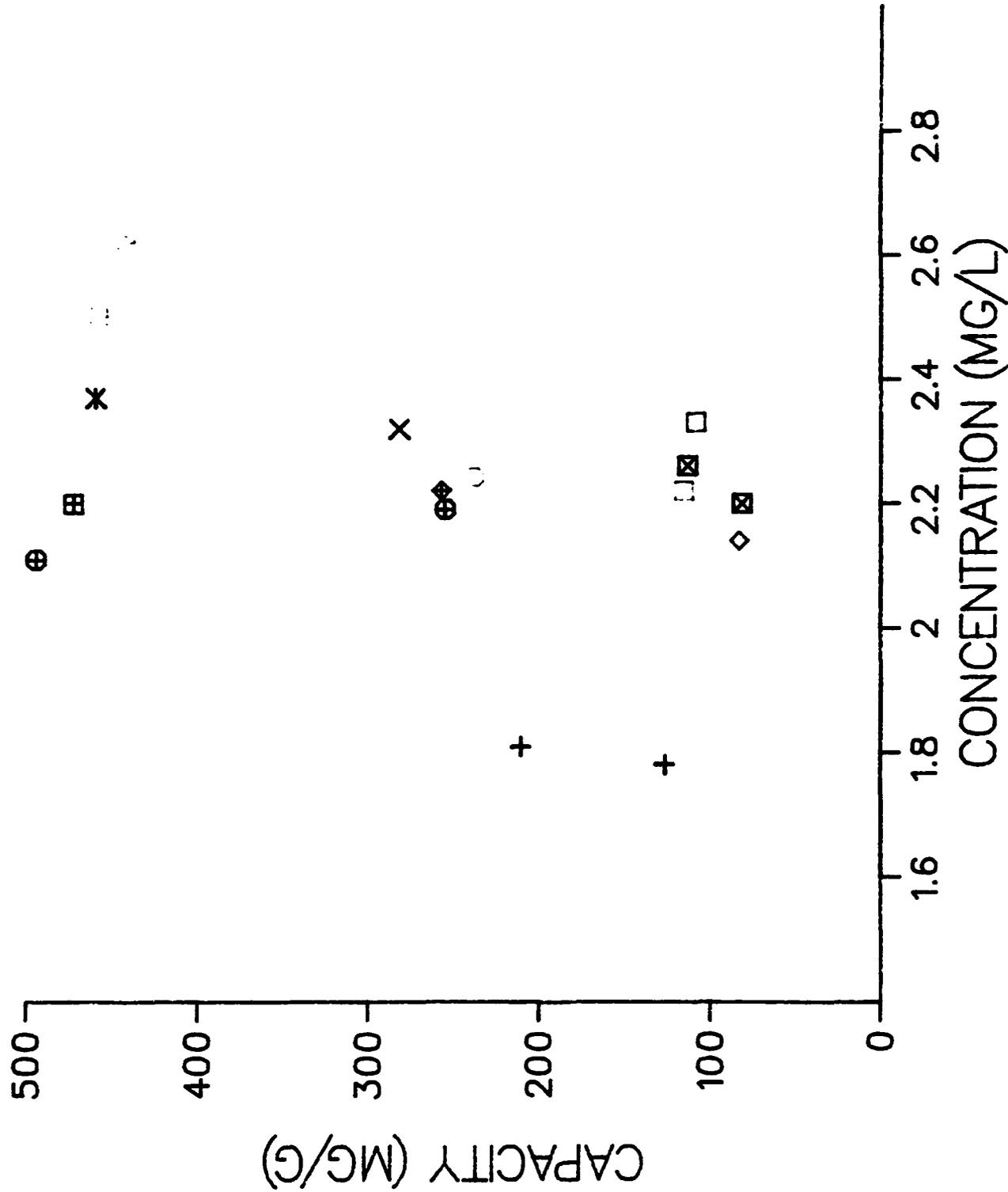
clusters of points. Adsorbent P-12 appears to be divided between the lower group and the middle group and adsorbent P-10 appears to be divided between the upper and the middle group. These variation in the dynamic capacities for these two adsorbents are difficult to explain and are unresolved. The grouping of the various adsorbents are explainable based on the individual adsorbents respective formulations and will be addressed in the companion synthesis volume. The two adsorbents in the upper group with the highest capacities may be unusually good materials or may show high capacity as a result of the high challenge concentrations. This result should be explored further.

The macronet adsorbents that are listed in Table X show very good capacity for DMMP and are located in the highest capacity group in Figure 8. These results are in agreement with those results that were reported earlier(26).

2. High Humidity Screening Studies.

The results of the screening studies performed at high relative humidity are tabulated in Table XI. and plotted against concentration in Figure 9. The method and time used to condition adsorbents prior to challenging them with the humid DFP stream are varied. The results of experiments that challenged the adsorbents with DFP streams of two different relative humidities are presented.

Figure 9 shows a scatter pattern when the capacities are plotted against concentration. Furthermore, the results obtained with an intermediate level of humidity (50% RH) and scattered with the results obtained at high relative humidity (95%). The polymeric macroporous adsorbents appear to maintain a large part of or all of their dynamic capacity towards DFP under the conditions run. This includes conditioning of the adsorbents at the test humidity for a period of one, two, or three days prior to challenging.

The macronets, however, show more varied results. The macronet N-8 seems to show a dependence on the batch, the conditioning, or the challenge stream relative humidity. The material that was conditioned at 50% RH overnight prior to testing (N-8, Lot CH1308) had a much higher capacity than a similar sample (N-8, Lot SGM911) that had been conditioned with 97% RH for 20 hours before testing. Macronet N-9 maintained about 50% of it's dry capacity and the capacity in the humid stream was independent of length of time of conditioning or relative humidity of the challenge stream. However, N-5 and N-10 suffered severe loss of capacity in the humid streams. Macronet N-5 was conditioned statically for an unduly long time and was wet with liquid water when it was removed from the desiccator.

TABLE XI
DYNAMIC DFP TESTING (HIGH HUMIDITY)

SORBENT	SORBENT TYPE	RH (%)	CHALLENGE CONCENTRATION (mg/L)	BREAKTHROUGH TIME (min)	BREAKTHROUGH CAPACITY (mg/g)
JLM 4219 (P-10)	Macroporous	97	1.53	308	469
JLM 4219[1](P-10)	Macroporous	50	1.25	220	275
EJL 595[2] (P-1)	Macroporous	50	1.40	179	242[*]
SGM 767[5] (P-2)	Macroporous	97	1.18	289	336
SGM 755[3] (N-5)	Macronet	50	1.30	26	31[†]
CH 1308[1] (N-8)	Macronet	50	1.27	681	861
SGM 911[4]	Macronet	97	1.57	90	141
SGM 917[1] (N-10)	Macronet	97	2.07	21	43
SGM 1003[4]	Macronet	97	1.14	267	240
SGM 1003[6](N-9)	Macronet	97	1.18	187	220
SGM 1003[4]	Macronet	56	0.66	318	236
BPL[1]	Carbon	50	1.34	171	218
Whetlerite[1]	Carbon	50	1.42	97	133

[1] Humidified overnight in stream of running humidity

[2] Humidified 2 days in stream of running humidity

[3] Humidified 6 months in a desicator

[4] Humidified 20 hrs. in a stream of running humidity

[5] Humidified 3 days in a stream of running humidity

[6] Humidified 91 hrs. in a stream of running humidity

[*] High background

[†] Sample dripping wet humidified in desicator 6 months

FIGURE 9.

DYNAMIC DFP CAPACITY OF ADSORBENTS UNDER HUMID CONDITIONS

Legend
△ P—1
✕ P—2(SGM767)
□ P—10
☒ N—5
▨ N—8(1308)
✳ N—8(SGM911)
◆ N—10
⊕ N—9
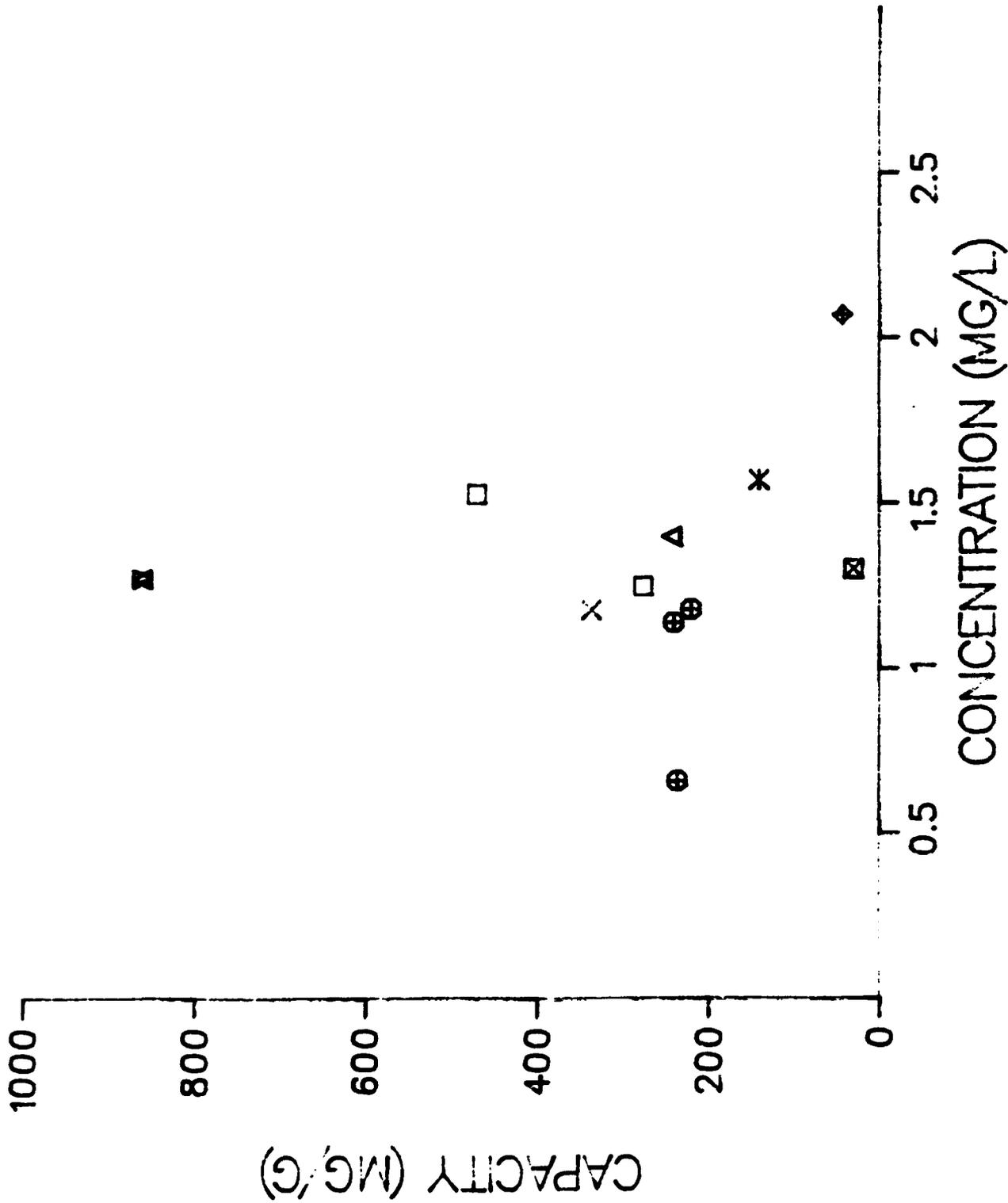
The macronet N-10 showed a loss of it's ability to sorb DFP from the humid stream after conditioning overnight. Macronet N-10 though, picked up the most water of any of the macronets in the water isotherm measurements.

Table XI also contains DFP dynamic capacities for BPL carbon and ASC Whetlerite under 50% RH streams. In both cases, the adsorbent was humidified dynamically overnight at the humidity of the challenge stream. These results indicate that the BPL carbon looses 25% (dry BPL challenged in a dry stream has a breakthrough capacity of 290 mg/g) and the ASC Whetlerite looses 36% (dry ASC Whetlerite has a breakthrough capacity of 209 mg/g) of their dry dynamic capacity under our test conditions.

Clearly, the humidity measurements taken up during this study are not definitive or complete. They merely represent an indication of what can be expected of the adsorbents under humid conditions and further work should be carried out to more rigorously define the efficacy of the synthetic adsorbents and ASC Whetlerite under highly humid conditions.

3. Adsorbent Selection

From all the samples that were prepared and screened under this program, it is obvious that some selection criteria must be used to determine which samples are carried through for a more thorough evaluation. The results presented above indicate that the synthetic adsorbents of lower mercury intrusion volumes have lower dynamic capacities for the simulant DMMP as shown in Figure 10. The adsorbents P-4, P-5, and P-16 each have a low mercury intrusion volume and also have low DMMP capacity. Adsorbents P-6 and P-7 appear to have very high dynamic capacity for the mercury intrusion volumes of these adsorbents and they will be investigated further. However, details of sorbent selection are contained in the proprietary synthesis volume. The adsorbents that were chosen for further study are the polymeric macroporous adsorbents P-2, P-10, P-11, P-12, and the polymeric macronet N-8. Adsorbents P-6 and P-7 will be considered in the future.

Inspection of the screening data suggests that there is a possibility of sample to sample variability within the different batches of each adsorbent type. In order to minimize the effect of batch variations, several batches of each adsorbent selected were combined to form a blend of that particular resin type. Each blend would then be evaluated in more detail using the bed depth service time (BDST) method. The data characterizing the individual batches of each adsorbent and the adsorbent blend of that batch are given in Table XII. Inspection of this data shows that there is very good reproducibility in the characterization data from batch to batch.

FIGURE 10.

DYNAMIC DMMP CAPACITY OF MACROPOROUS ADSORBENTS
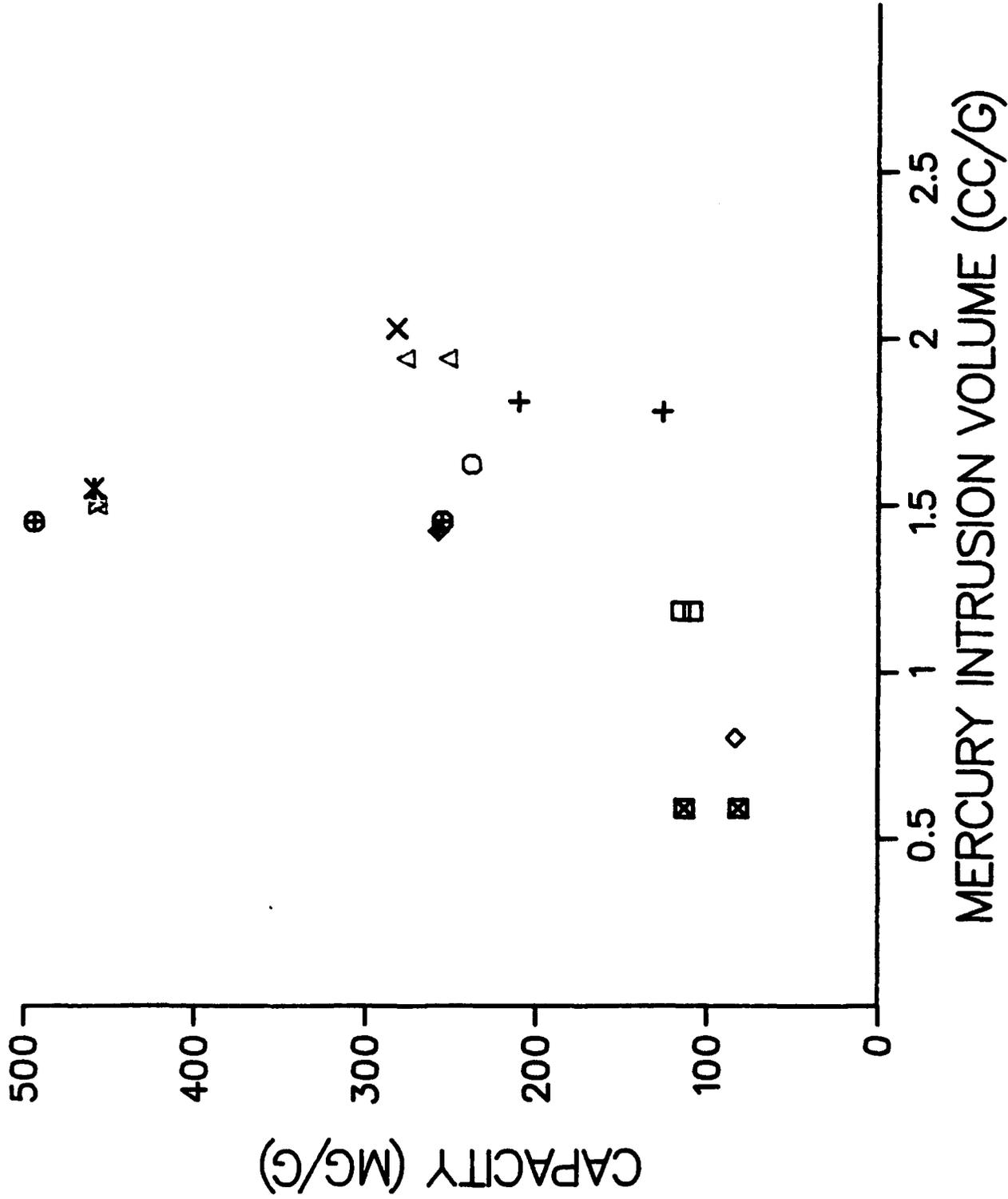
Legend
- △ P−2(CH1220)
- ✕ P−2(JLM4245)
- □ P−4
- ⊠ P−5
- ⊠ P−6
- ✕ P−7
- ◆ P−8
- ⊕ P−10
- ○ P−11
- + P−12
- ◇ P−16

TABLE XII

CHARACTERIZATION OF BLENDS

Adsorbent	Lot Number	BET Surface Area (m^2/g)	Hg Intrusion Volume (cc/g)
P-2 Blend	JLM4537-2	759(800+20)[*]	(1.57+0.15)[*]
	JLM4525-1	817	1.57
	JLM4525-2	819	1.72
	JLM4527-1	786	1.37
	JLM4527-2	781	1.62
P-10 Blend	JLM4537-5	(885+58)[*]	(1.40+0.05)[*]
	JLM4539-1	811	1.32
	JLM4539-2	870	1.44
	JLM4541	913	1.41
	JLM4543	946	1.42
P-11 Blend	JLM4537-3	840(828+36)[*]	(1.59+0.10)[*]
	JLM4521-1	834	1.65
	JLM4521-2	861	1.65
	JLM4523	789	1.47
P-12 Blend	JLM4537-1	847(840+16)[*]	1.37(1.38+0.02)
	JLM4511	821	1.39
	JLM4517-2	838	1.40
	JLM4519-1	860	1.37
	JLM4519-2	841	1.35
N-8 Blend	JLM4537-4	1335(1330+110)[*]	0.65
	JLM4531-1	1271	-
	JLM4531-2	1271	-
	JLM4533	1458	-

[*] Average of values determined on individual batches.

C.   JONAS-HUTCHINS BED DEPTH SERVICE TIME TREATMENT (BDST)

The BDST treatment was first proposed by Jonas (57,58) and by Hutchins (59) as a laboratory method to generate data to permit the design of packed bed adsorbers. The method allows a means of predicting the effects of flow rates and challenge concentrations on the performance of an adsorbent in a fixed bed adsorber. Jonas' work is based on the work of Wheeler (60,61). Although Hutchins' paper deals with purification of aqueous streams it is based on the work of Bohart and Adams (62), Klotz (63), and Dole and Klotz (64) each of which deals with the removal of sorbates from gaseous streams. The method was recently used by Staginnus (65) to describe the adsorption of cyanogen chloride and chloropicrin on activated carbon.

The BDST method consists of determining the breakthrough times as a function of bed depth of an adsorbent that is challenged with a fluid containing a fixed level of organic sorbate. If a column exhibits constant pattern behavior(66-70) and constant values of Co, Cx, ρB, Q, and temperature, a plot of lifetime vs bed depth is usually linear and can be represented by the equation:

$$t_b = \frac{W_e \rho_B A}{C_o Q} \, x - \frac{\rho_B}{k_v} \ln \frac{C_o}{C_x} \qquad (4)$$

where tb is the breakthrough time (min)(71) at which the concentration of the adsorbate in the effluent stream is equal to Cx (g/cm3), Co is the concentration of the adsorbate in the influent stream (g/cm3), Q is the volumetric flow rate (cm3/min), B is the bulk density of the adsorbent in the packed bed, kv is the pseudo first order adsorption rate constant (min-1), W is the adsorbent weight (g), We is the kinetic saturation capacity (g/g) at a specified ratio of Cx/Co. The slope, m, is the reciprocal of the speed at which the adsorption front moves through the packed bed, S in cm/min, and is equal to:

$$m = \frac{W_e \rho_B A}{C_o Q} = \frac{1}{S} \qquad (5)$$

The intercept of the equation is:

$$b = \frac{W_e \rho_B Q}{k_v} \ln \frac{C_o}{C_x} \qquad (6)$$

According to the mass transfer zone (MTZ) model of column performance (68-70), all of the adsorbate contained in the influent stream is adsorbed onto the adsorbent prior to breakthrough (70,72). Consequently, the rate of feed of the adsorbate to the column is equal to the rate of exhaustion of the adsorbent in the column. Since the rate of feed, rF is:

$$rF = (Co)(F) \tag{7}$$

where Co is the influent concentration of adsorbate in mg/L, F is the flow rate in L/min, and the rate of exhaustion of the adsorbent bed, rE, is:

$$rE = (S)(We)(\rho B)(A) \tag{8}$$

where S is defined above, Ls is the loading of the adsorbent at saturation in mg/g, ρB is the bulk density of the adsorbent in g/cm3, and A is the cross-sectional area of the column (cm2), it follows that by equating (5) and (6) and rearranging that:

$$We = (CoF)/S\rho BA \tag{9}$$

which is the identical result that was obtained above.

1. Low Humidity BDST

The BDST studies were performed in the same manner as the screening studies described previously. The ASC Whetlerite was removed from a vacuum sealed canister and stored under vacuum. The synthetic adsorbents were not preconditioned in any way but were used as they were removed from the bottle in which they were stored. Breakthrough times were measured as a function of the bed depth of the adsorbent using the gas chromatograph. The boiling points, average challenge concentration, and average P/Po values for the adsorbates used are listed in Table XIII. The breakthrough times were then normalized to a challenge concentration of 2 mg/L. These data are contained in Tables XIV thru XIX. The breakthrough times were then normalized to a challenge concentration of 2 mg/L and plotted against the bed depth of the adsorbent as shown in Figures 11 thru 16.

The results of the BDST treatment that were calculated from the data plotted in Figures 11 thru 16 are shown in Table XX for the adsorbates methylene chloride, toluene, o-xylene, DMMP, DFP, and CIS. The methylene chloride data is only for the adsorbents ASC Whetlerite and the macronet N-8 because of the adsorbents studied, these are the only adsorbents that showed a measurable dynamic capacity. In general, the kinetic

saturation capacities of the synthetic adsorbents for the non-volatile adsorbates are two to three times that obtained for ASC Whetlerite. However, the kinetic saturation capacities of the macroporous synthetic adsorbents are much lower than that obtained with ASC Whetlerite for the volatile adsorbates methylene chloride, toluene, and o-xylene. The synthetic macronet adsorbents showed equal to or better kinetic saturation weight capacities than ASC Whetlerite in all cases except methylene chloride.

The volume capacity of the synthetic macronet adsorbent N-8 is equivalent to or higher than that obtained with ASC Whetlerite in all cases except methylene chloride. However, the volume capacities of the synthetic macroporous adsorbents are much lower than that obtained with ASC Whetlerite for the volatile adsorbents methylene chloride, toluene, and o-xylene and are comparable to ASC Whetlerite for the nonvolatile adsorbates DMMP, DFP, and CIS. The reason for the low volume capacities of the synthetic adsorbents relative to the weight capacities is a much lower and therefore less favorable bulk density than ASC Whetlerite. The bulk densities of the synthetic polymeric adsorbents range from 0.226 g/cc (P-2) to 0.386 g/cc (N-8) where as the bulk density of ASC Whetlerite is 0.57 g/cc.

The performance of the synthetic macroporous adsorbents appears to be independent of the formulation of the adsorbents. This is only the case in the range of formulations of macroporous adsorbents studies by the BDST technique since screening studies described previously have shown that other macroporous adsorbents have lower capacities for the adsorbates DFP and CIS. This indicates that the macroporous adsorbent of choice would be the one with the highest bulk density which would increase the attrition resistance by lowering the porosity. The resin of choice would then be P-12 because of the higher bulk density and attrition resistance as well as a more readily available raw material.

Figure 17 is a plot of the kinetic saturation capacities of the adsorbents tested against the boiling point of the adsorbate at 760 torr. An excellent correlation is obtained for ASC Whetlerite (correlation coefficient, r=0.9987, 4 points). The crossover point where the kinetic saturation capacity of P-11 becomes greater than that for ASC Whetlerite is 129 C. For adsorbates with boiling points above 129 C, P-11 should have a kinetic saturation capacity that is greater than that of ASC Whetlerite.

The macronet adsorbent also shows a rough correlation (correlation coefficient, r= 0.9671, 6 points) but the points are more scattered and the fit is not as good as with ASC Whetlerite or P-11. This is probably because the adsorbent is not conditioned in any way prior to use. However, the least squares fitted line crosses the ASC Whetlerite line at a tb of 74 C. This indicates that N-8 should have a higher kinetic saturation capacity for adsorbates with boiling points greater than 74 C.

The remaining synthetic adsorbents do not show good correlations with the boiling points of the adsorbates. This is again probably due to a lack of conditioning of the adsorbent prior to use. We will continue to refine the data to try to develop the correlations for the remaining polymeric adsorbents.

These correlations are reminiscent of Trouton's rule (75) which points out that enthalpies of vaporization increase almost linearly with normal boiling point. Although the enthalpy of vaporization is not the same as the enthalpy of adsorption, the correlation probably indicates that the adsorption phenomenon and condensation phenomenon are closely related and utilize similar forces. The correlations are similar to the dependency of adsorption capacity of carbon for gasses with the critical temperature of the adsorbate (76).

TABLE XIII

PHYSICAL PROPERTIES AND AVERAGE CHALLENGE CONCENTRATIONS OF ADSORPTIVES

Adsorbate	Boiling Point (C)	Average Challenge Concentration (mg/L)	Average P/P_o at 20 C
Methylene Chloride	40	2.57+0.14	0.00160[3]
Toluene	110	5.14+0.48	0.0488[3]
o-Xylene	144	3.79+0.24	0.133[3]
DMMP	181	2.24+0.26	0.379[4,5]
DFP	183[1]	2.15+0.23	0.369[1,4]
CIS	188[1]	1.47+0.40	-

TABLE XIV

BDST DATA FOR THE ADSORPTIVE METHYLENE CHLORIDE AT LOW HUMIDITY

Adsorbate	Sorbent Weight (g)	Bed Height (min)	Challenge Concentration (mg/L)	Breakthrough	
				Time (min)	Capacity (mg/g)
ASC	1.8255	38	2.40	45	59
ASC	2.6628	52	2.70	81	82
ASC	4.0304	76	2.70	143	96
N-8	1.3677	38	2.40	9	16
N-8	1.8196	52	2.40	12	16
N-8	2.7037	76	2.51	17	16

TABLE XV

BDST DATA FOR THE ADSORPTIVE TOLUENE AT LOW HUMIDITY

Adsorbent	Sorbent Wt (g)	Bed Ht (mm)	Challenge Concentration (mg/L)	Breakthrough Time (min)	Breakthrough Capacity (mg/g)
ASC Whetlerite	0.5893	14	5.83	9	89
	1.0944	23	5.85	39	208
	1.6352	40	5.70	60	209
	2.6053	53	5.85	92	206
N-8(JLM4515)	0.4591	14	5.70	<3	<37
	0.9160	25	5.70	18	112
	2.8166	76	5.80	110	227
P-2(SGM767)	0.7563	37	4.96	9	59
	0.9850	48	4.61	15	70
	1.7258	97	4.94	41	117
P-10(JLM4503)	1.0042	45	5.20	12	62
	1.1542	52	4.70	18	73
	1.2294	66	4.65	21	79
	2.0200	91	4.70	41	95
P-11(JLM4523)	1.0114	50	5.30	12	63
	1.5627	75	5.15	23	76
	1.8927	92	5.15	30	82
P-12(JLM4517)	1.0895	48	4.90	14	66
	1.5479	68	5.30	21	72
	2.1000	91	5.05	33	79
BPL Carbon	1.0461	25	4.65	42	187
	2.2151	51	4.65	119	250
	3.2812	76	4.80	183	266

TABLE XVI

BDST DATA FOR THE ADSORPTIVE o-XYLENE
AT LOW HUMIDITY

Adsorbent	Sorbent Wt (g)	Bed Ht (mm)	Challenge Concentration (mg/L)	Breakthrough Time (min)	Capacity (mg/g)
ASC Whetlerite	1.8545	38	3.79	66	135
	2.5905	52	3.79	119	174
	3.7202	78	3.82	247	254
ASC Whetlerite[1]	2.1789	38	3.77	60	103
	2.9555	52	3.55	104	125
	4.5705	78	3.55	214	166
N-8(JLM4537-4)	1.3902	38	3.83	61	168
	1.7238	52	3.83	166	369
	2.6153	78	4.00	340	520
N-8(JLM4537-4)[1]	1.3762	38	3.79	68	187
	1.8652	52	3.79	109	221
	2.7118	78	3.83	143	202
P-2(JLM4537-2)	0.7884	38	3.45	6	26
	1.0606	52	3.30	12	37
	1.5559	78	4.00	47	120
P-10(JLM4537-5)	0.8322	38	4.00	11	58
	1.1146	52	3.88	26	90
	1.7118	78	3.88	55	125
P-11(JLM4537-3)	0.7092	38	3.80	17	91
	0.9588	52	3.80	33	130
	1.5183	76	3.80	87	216
P-12(JLM4537-1)	0.8484	38	3.45	6	24
	1.1170	52	3.45	14	43
	1.8073	76	3.30	33	60

[1] Adsorbent conditioned at ambient humidity.

TABLE XVII

BDST DATA FOR THE ADSORPTIVE DMMP
AT LOW HUMIDITY

Adsorbent	Sorbent Wt (g)	Bed Ht (mm)	Challenge Concentration (mg/L)	Breakthrough	
				Time (min)	Capacity (mg/g)
ASC Whetlerite	1.8507	38	1.80	325	316
	2.5441	52	1.91	462	347
	3.7506	76	2.15	562	322
N-8(JLM4537-4)	1.3287	38	2.19	519	855
	1.7789	52	1.90	779	833
	2.8135	76	2.08	1210	896
P-2(JLM4537-2)	0.7753	38	2.31	33	98
	1.0766	52	2.45	112	255
	1.5891	76	2.38	127	190
P-10(JLM4537-5)	0.8673	38	1.83	136	286
	1.1274	52	1.97	155	271
	1.8543	76	1.97	246	261
P-11(JLM4537-3)	0.7244	38	2.38	37	122
	0.9761	52	2.31	69	163
	1.5512	76	2.54	33	96
P-12(JLM4537-1)	0.8700	38	2.54	33	96
	1.1550	52	2.46	69	146
	1.6606	76	2.31	142	197

TABLE XVIII

BDST DATA FOR THE ADSORPTIVE DFP
AT LOW HUMIDITY

| Adsorbent	Sorbent Wt (g)	Bed Ht (mm)	Challenge Concentration (mg/L)	Breakthrough Time (min)	Capacity (mg/g)
ASC Whetlerite	1.2740	25	1.92	120	181
	2.5192	51	2.02	304	244
	3.7901	76	2.04	487	262
N-8(JLM4537-4)	1.4135	38	2.37	506	848
	1.8640	52	2.13	874	999
	2.7334	76	1.87	1322	904
P-2(JLM4537-2)	0.7964	38	2.30	101	291
	1.1093	52	2.20	199	394
	1.5985	76	2.08	398	474
P-10(JLM4537-5)	0.8434	38	2.43	164	473
	1.1345	52	1.90	279	467
	1.7452	76	2.08	398	474
P-11(JLM4537-3)	0.7778	38	2.45	114	359
	1.0078	52	1.95	170	329
	1.6050	76	2.19	324	442
P-12(JLM4537-1)	0.9193	38	2.21	222	412
	1.2324	52	2.20	276	473
	1.8515	76	1.75	382	361

TABLE XIX - BDST DATA FOR THE ADSORPTIVE CIS AT LOW HUMIDITY

Adsorbent	Sorbent Wt. (g)	Bed Ht. (mm)	Challenge Concentration mg/L	Breakthrough Time (min)	Breakthrough Capacity (mg/g)
ASC Whetlerite	1.3502	25.4	1.76	169	226
	2.6433	52	1.50	426	242
	3.1921	64	1.57	548	270
	3.8992	76	1.47	709	267
N-8(JLM4515)	1.4602	38	1.76	444	535
	1.9062	52	1.46	872	668
	2.8541	76	1.40	1413	703
N-8(JLM4537-4)	1.3310	38	1.10	635	534
	1.8121	52	1.06	1020	597
	2.7352	76	1.22	1476	658
P-2(SGM767)	0.7623	38	1.27	210	350
	0.9654	52	1.44	266	396
	1.5143	76	1.64	363	393
P-2(JLM4537-2)	0.7802	38	1.18	160	242
	1.0600	52	1.57	224	332
	1.6315	76	1.43	399	349
P-10(JLM4537-5)	0.8980	38	1.60	207	369
	1.8320	76	1.47	457	367
P-11(JLM4523	0.7213	38	1.69	105	246
	1.0411	52	1.69	185	300
	1.5061	76	1.69	370	415
P-12(JLM4517)	0.8548	38	1.32	210	324
	1.0411	52	1.40	284	355
	1.5061	76	1.49	480	412
P-12(JLM4537-1)	0.8882	38	1.29	164	238
	1.1682	52	1.21	249	258
	1.7905	76	1.11	515	316

FIGURE 11.

BED DEPTH SERVICE TIME (BDST) PLOT FOR METHYLENE CHLORIDE
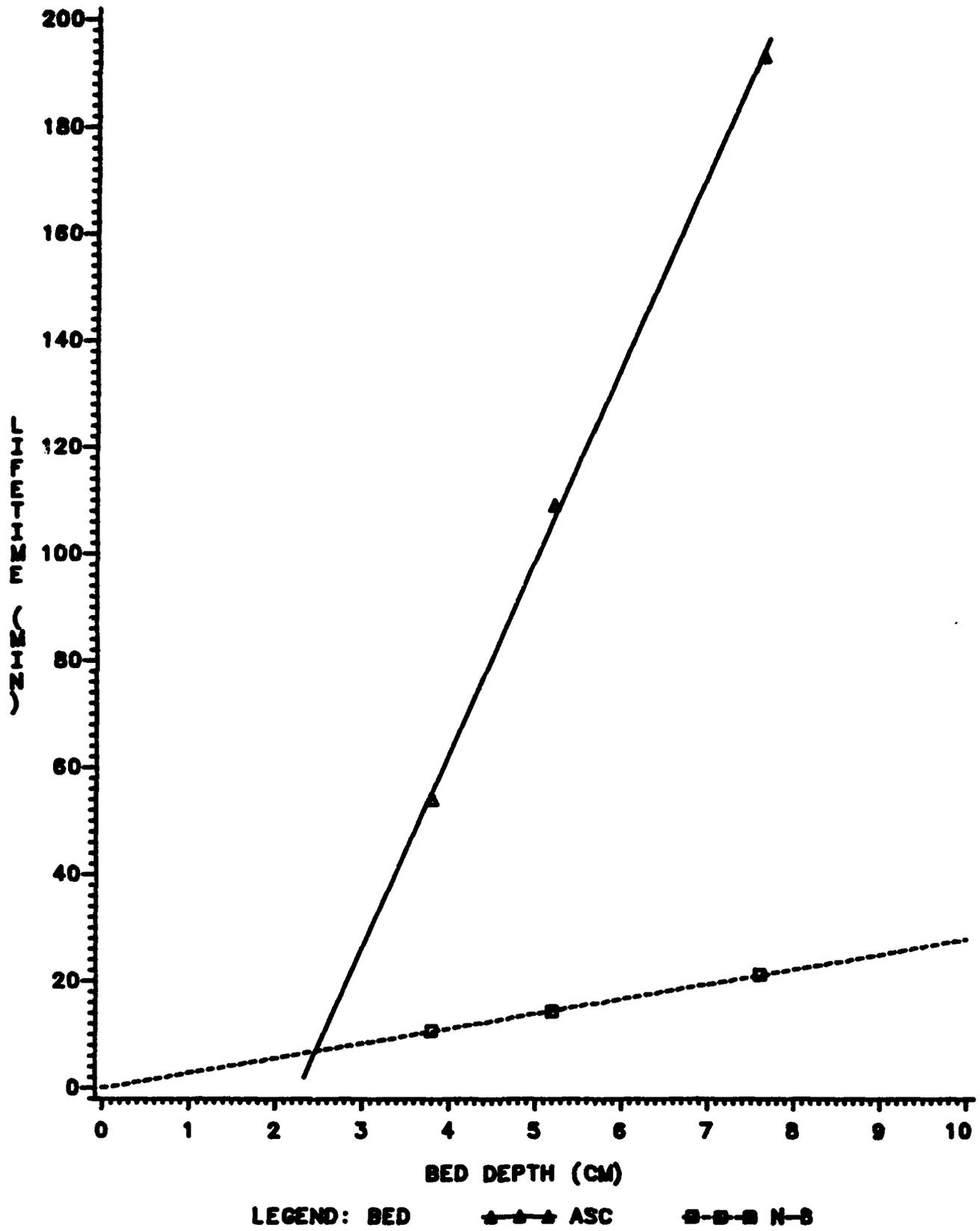
LEGEND: BED   ▲—▲—▲ ASC   ▣—▣—▣ N—B

TOLUENE BED DEPTH SERVICE TIME (BDST) PLOT
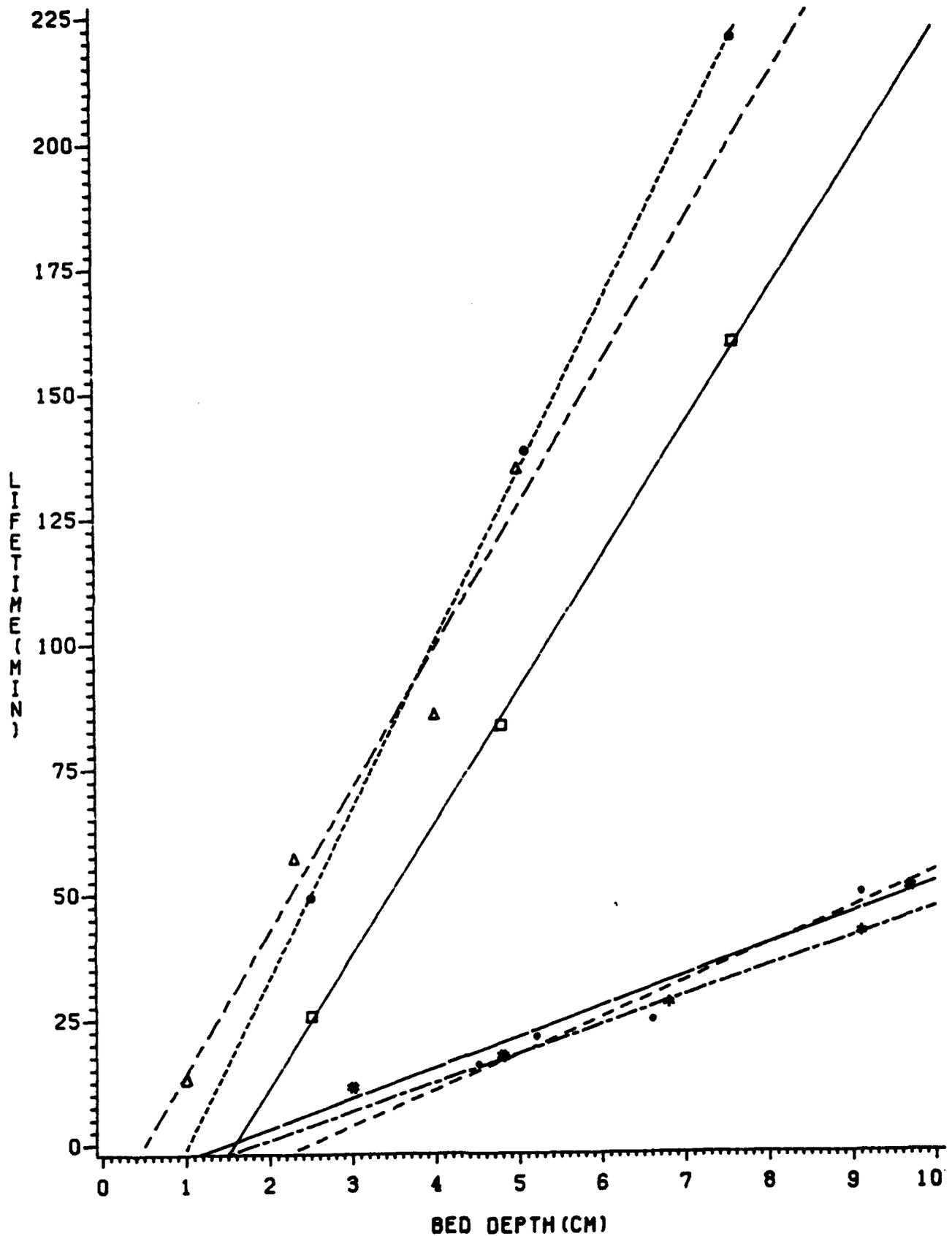
LEGEND: BED   ▲-▲-▲ ASC   ●-●-● BPL   ⊟-⊟-⊟ JLM4515
                ✦-✦-✦ JLM4517   ✦-✦-✦ P-10   ◆-◆-◆ SGM767

BED DEPTH SERVICE TIME (BDST) PLOT FOR O–XYLENE
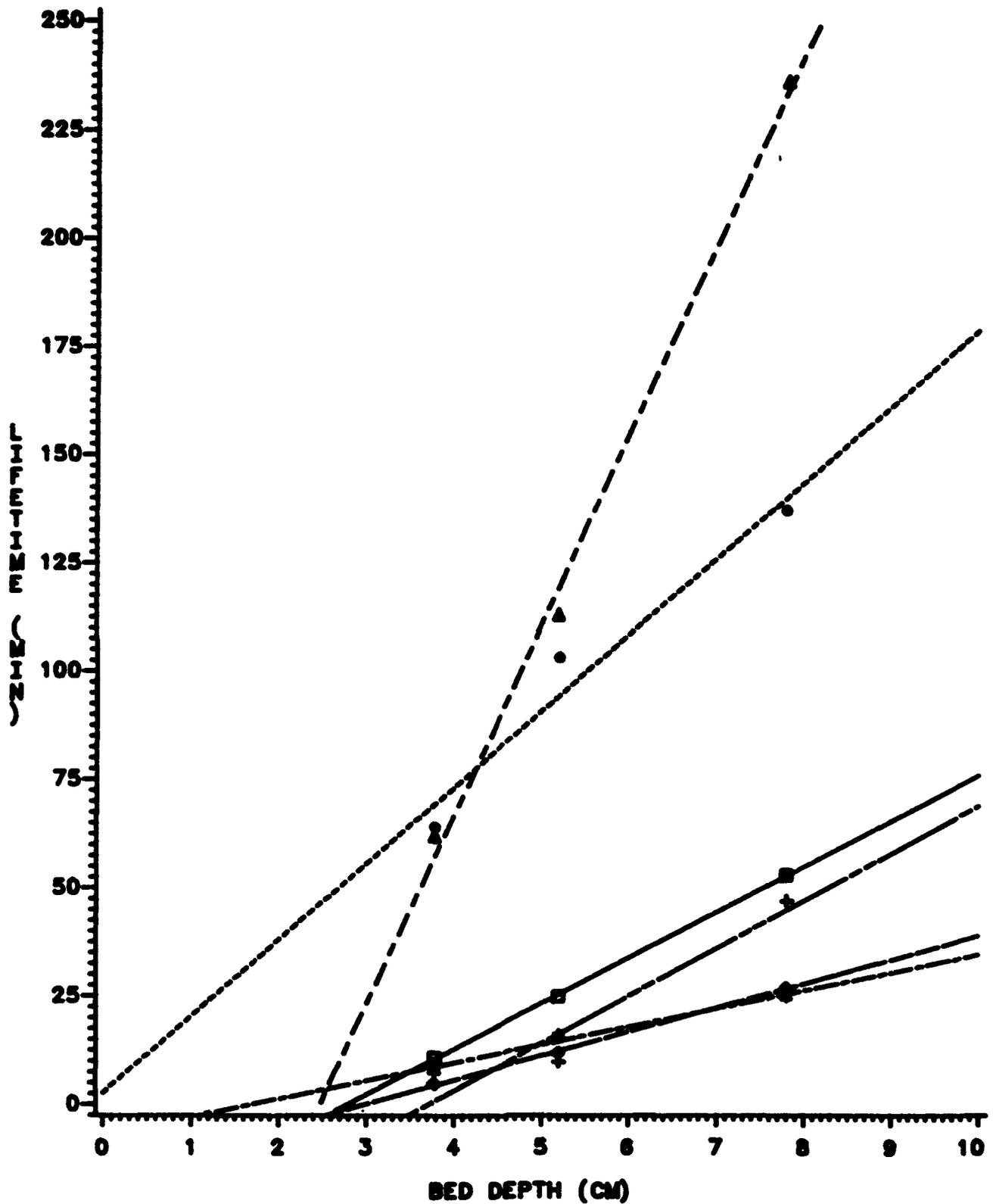
LEGEND: BED   ▲ ▲ ▲ ASC   ◆ ◆ ◆ N–8   ■ ■ ■ P–10
              ◆ ◆ ◆ P–11   ◆ ◆ ◆ P–12   + + + P–2

BED DEPTH SERVICE TIME (BDST) PLOT FOR DMMP

BED DEPTH SERVICE TIME (BDST) PLOT FOR DFP

FIGURE 16.

CIS BED DEPTH SERVICE TIME (BDST) PLOT
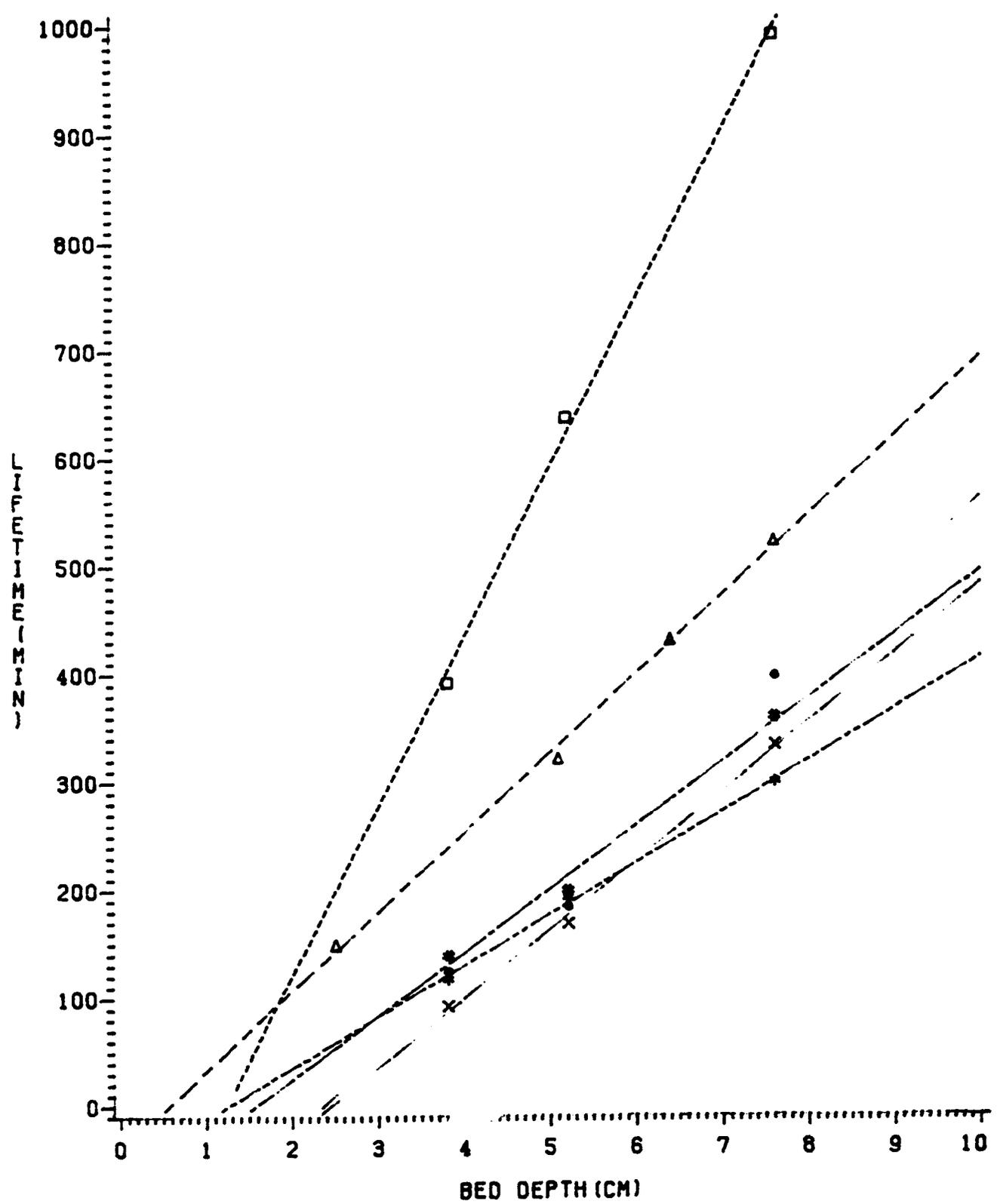
TABLE XX - RESULTS OF BDST TREATMENT OF THE DYNAMIC DATA AT LOW HUMIDITY

| Adsorbent	Challenge Vapor	Regression Equation $tb=aDo+b$	Correlation Coefficient	Critical Bed Depth DC (cm)	Rate of Adsorption Front, S (cm/min)	Kinetic Saturation Capacity Ls mg/g	mg/mL
ASC Whetlerite	Methylene Chloride	36.4 Do-82.8	0.9995	2.3	0.02747	164	93
N-8 (JLM4537-4)	Methylene Chloride	2.78Do+ 0.144	0.9995	-0.5	0.3603	18.4	7
BPL Carbon	Toluene	33.5 Do-34.2	0.9999	1.0	0.0299	325	172
ASC Whetlerite	Toluene	28.9 Do-21.2	0.9830	0.8	0.0346	260	148
N-8 (JLM4515)	Toluene	26.4 Do-41.4	0.9997	1.6	0.0379	350	135
P-2 (SGM767)	Toluene	6.64Do-13.9	0.9996	2.1	0.151	150	33.9
P-10 (JLM4503)	Toluene	7.17Do-17.9	0.9741	2.7	0.140	140	35.7
P-11 (JLM4523)	Toluene	5.41Do-11.1	1.0000	2.1	0.185	120	27.7
P-12 (JLM4517)	Toluene	5.71Do-10.5	0.9993	1.8	0.175	113	29.3
ASC Whetlerite	O-xylene	44.0 Do-109	0.9980	2.5	0.0227	396	226
N-8 (JLM4537-4)	O-xylene	17.6 Do- 2.79	0.9778	0.1	0.00169	786	303
P-2 (JLM4537-2)	O-xylene	9.47Do-29.0	0.9619	3.2	0.1056	275	62.1
P-10 (JLM4537-5)	O-xylene	10.5 Do-29.3	0.9998	2.8	0.0950	212	54.1
P-11 (JLM4537-3)	O-xylene	4.15Do- 6.91	0.9906	1.7	0.241	92.1	21.3
P-11 (JLM4537-3)	O-xylene	18.1 Do-56.6	0.9875	3.2	0.05534	401	93.6
P-12 (JLM4537-1)	O-xylene	5.53Do-16.3	0.9994	3.0	0.1808	110	28.5
ASC Whetlerite	DMMP	80.6 Do- 0.146	0.9922	0.009	0.01241	362	206
N-8 (JLM4537-4)	DMMP	186Do-172	0.9913	1.0	0.005482	1212	468
P-2 (JLM4537-2)	DMMP	30.2 Do-80.6	0.9955	2.7	0.0331	343	77.5
P-10 (JLM4537-5)	DMMP	31.7 Do- 2.44	0.9909	0.2	0.03155	319	81.3
P-11 (JLM4537-3)	DMMP	28.6 Do-66.2	0.9992	2.3	0.0350	317	73.2
P-12 (JLM4537-1)	DMMP	32.2 Do-81.1	0.9998	2.5	0.0311	318	82.4
ASC Whetlerite	DFP	74.9 Do-73.2	1.000	1.0	0.0134	336	192
N-8 (JLM4537-4)	DFP	163Do+29.4	0.9848	0.04	0.0061	1090	421
P-2 (JLM4537-2)	DFP	58.9 Do-99.7	0.9953	1.7	0.0170	667	151
P-10 (JLM4537-5)	DFP	57.2 Do-23.7	0.9977	0.4	0.0175	574	146
P-11 (JLM4537-3)	DFP	59.0 Do-106	0.9659	1.8	0.0169	656	152
P-12 (JLM4537-1)	DFP	22.3 Do-171	0.9479	-6.4	0.0448	220	57.0

TABLE XX — RESULTS OF BDST TREATMENT OF THE DYNAMIC DATA AT LOW HUMIDITY (contd.)

Adsorbent	Challenge Vapor	Regression Equation $tb=aDo+b$	Correlation Coefficient	Critical Bed Depth DC (cm)	Rate of Adsorption Front, S (cm/min)	Kinetic Saturation Capacity Ls mg/g	mg/mL
ASC Whetlerite	CIS	73.1 Do-39.7	0.9985	0.6	0.0137	328	187
N-8 (JLM4515)	CIS	156 Do-193	0.9989	1.2	0.00640	1040	401
N-8 (JLM4537-4)	CIS	146 Do-208	0.9997	1.4	0.00687	967	373
P-2 (SGM767)	CIS	43.5 Do-33.0	0.9999	0.76	0.0230	493	111
P-2 (JLM4537-2)	CIS	49.6 Do-89.6	0.9977	1.8	0.0202	562	127
P-10 (JLM4503)	CIS	73.4 Do-172	0.9870	2.4	0.0136	739	188
P-10 (JLM4537-5)	CIS	-	-	-	-	-	-
P-11 (JLM4523)	CIS	63.8 Do-156	0.9984	2.4	0.0157	707	163
P-11 (JLM4537-3)	CIS	59.6 Do-144	0.9970	2.4	0.0168	661	153
P-12 (JLM4517)	CIS	58.6 Do-92.0	0.9945	1.6	0.0171	579	150
P-12 (JLM4537-1)	CIS	48.0 Do-85.2	0.9917	1.8	0.0208	476	123

DEPENDENCE OF CAPACITY ON BOILING POINT
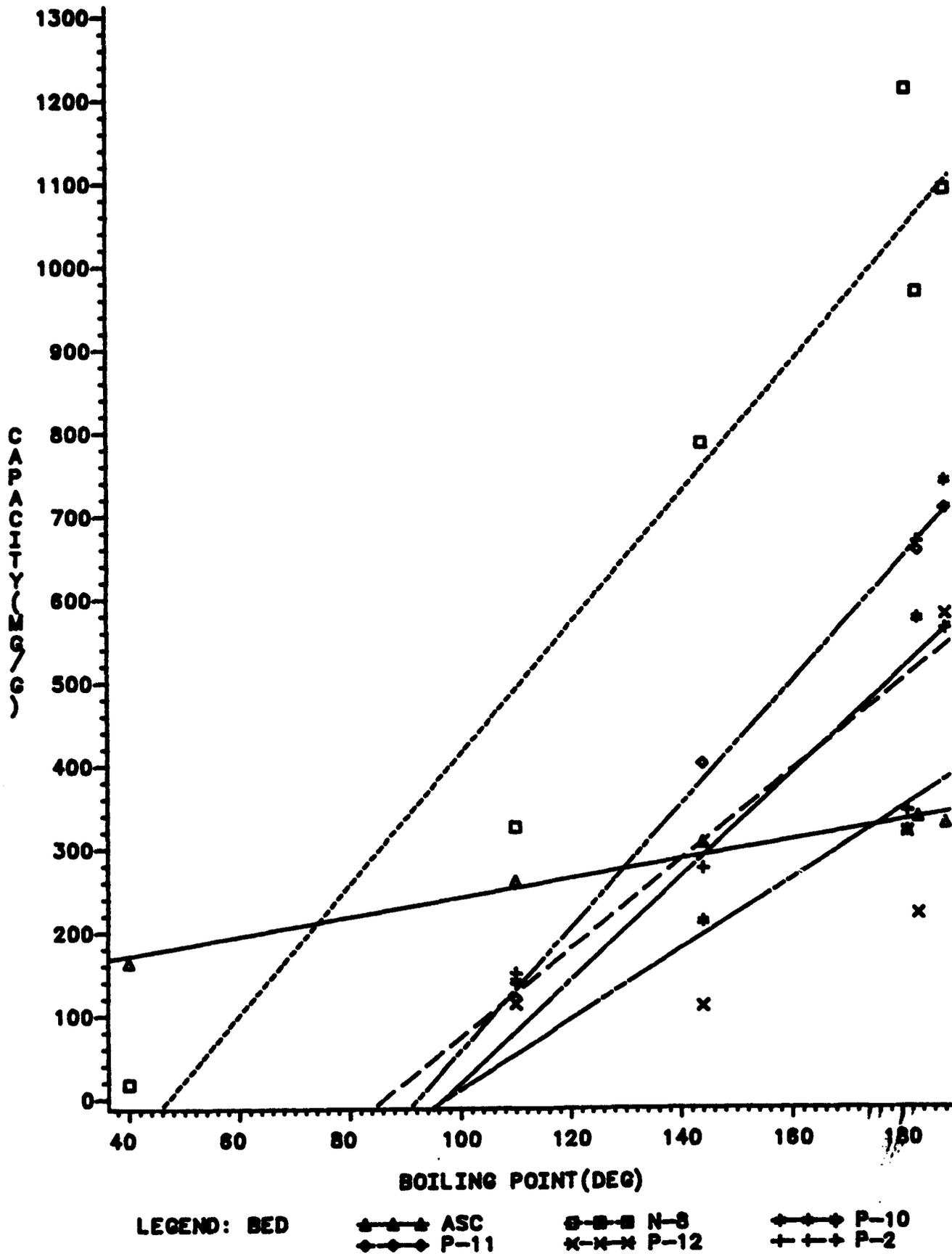
2. High Humidity Testing with DFP

All of the work described above was performed at low humidity. The Navy, however, operates in conditions of high humidity where an adsorbent may be fouled by preadsorbed moisture or where competitive adsorption must take place. We therefore wanted to find out if the ASC Whetlerite does indeed lose its capacity to adsorb organic vapors from flowing air streams as suggested by Nelson (6,77) for carbon and what effect humidity has on the ability of the synthetic polymeric adsorbents to adsorb organic vapors from air streams.

The ASC Whetlerite was humidified dynamically under a 95% RH air stream that was prepared by passing the air stream through a Fisher-Miligan gas washing jar containing deionized water. The relative humidity of the resulting stream was monitored using a Humicap 14 relative humidity indicator which had been calibrated over a saturated solution of potassium sulfate (RH = 97%) (56). The weight of water taken up as a function of time, amount of ASC Whetlerite, and flow rate are tabulated in Table XXI. When these data are plotted as shown in Figure 18, it becomes apparent that the time required for the ASC Whetlerite to reach kinetic saturation is dependent on the amount of ASC Whetlerite and flow rate.

Table XXII summarizes the ASC Whetlerite conditioning data and contains time required for kinetic saturation, the kinetic saturation capacity, and the linear flow. The time required to saturate an ASC Whetlerite bed with water under dynamic conditions is dependent on the flow rate through the bed since a plot of time to kinetic saturation vs linear flow is linear as shown in Figure 19. The correlation is reasonable (r = 0.9968) considering the precision involved in extracting the times to saturation from Figure 18 and the uncertainties in packing of the bed.

The kinetic saturation capacities of the three runs are very consistent at $311 + 13$ mgH_2O/g ASC Whetlerite. Since the area of a water molecule (78) is 10.6 A^2, the surface area of a 311 mg water monolayer is 1100 m^2/. This number is larger than the measured nitrogen BET surface area of ASC Whetlerite (804 m^2/g) which means that there is multilayer adsorption and probably capillary condensation which is in agreement with results found in the literature (79-84).

TABLE XXI

DYNAMIC WATER ADSORPTION BY
ASC WHETLERITE AT 95% RH

Sample Size (g)	Flow Rate (L/min)	Contact Time sec	Time min	Weight Gain (g)
1.0120	1	0.15	0	0
			50	0.2167
			110	0.2844
			170	0.2975
			230	0.3010
			290	0.3017
			350	0.3027
			410	0.3026
			470	0.3026
0.1159	1	1.06	0	0
			50	0.6567
			110	1.1643
			170	1.4779
			230	1.8338
			290	2.1011
			350	2.3777
			410	2.5992
			470	2.7481
			530	2.8991
			590	2.9928
			650	3.0610
			710	3.1119
			770	3.1443
			834	3.1708
			890	3.2039
			950	3.2312
			1010	3.2466
			1070	3.2563
			1505	3.2900
			1565	3.2889

TABLE XXI (Continued)

DYNAMIC WATER ADSORPTION BY
ASC WHETLERITE AT 95% RH

Sample Size (g)	Flow Rate (L/min)	Contact Time sec	Time min	Weight Gain (g)
9.6047	2	0.72	0	0
			60	1.0176
			120	1.5823
			180	2.1206
			240	2.5293
			300	2.7833
			360	2.8974
			420	2.9467
			480	2.9193
			600	2.9799
			660	2.9758
			720	2.9761
			780	2.9763

HUMIDIFICATION OF ASC WHETLERITE UNDER DYNAMIC CONDITIONS

LEGEND: WEIGHT   ▲–▲–▲ 1.012G   ▣–▣–▣ 10.1159G   ✦–✦–✦ 9.6047G
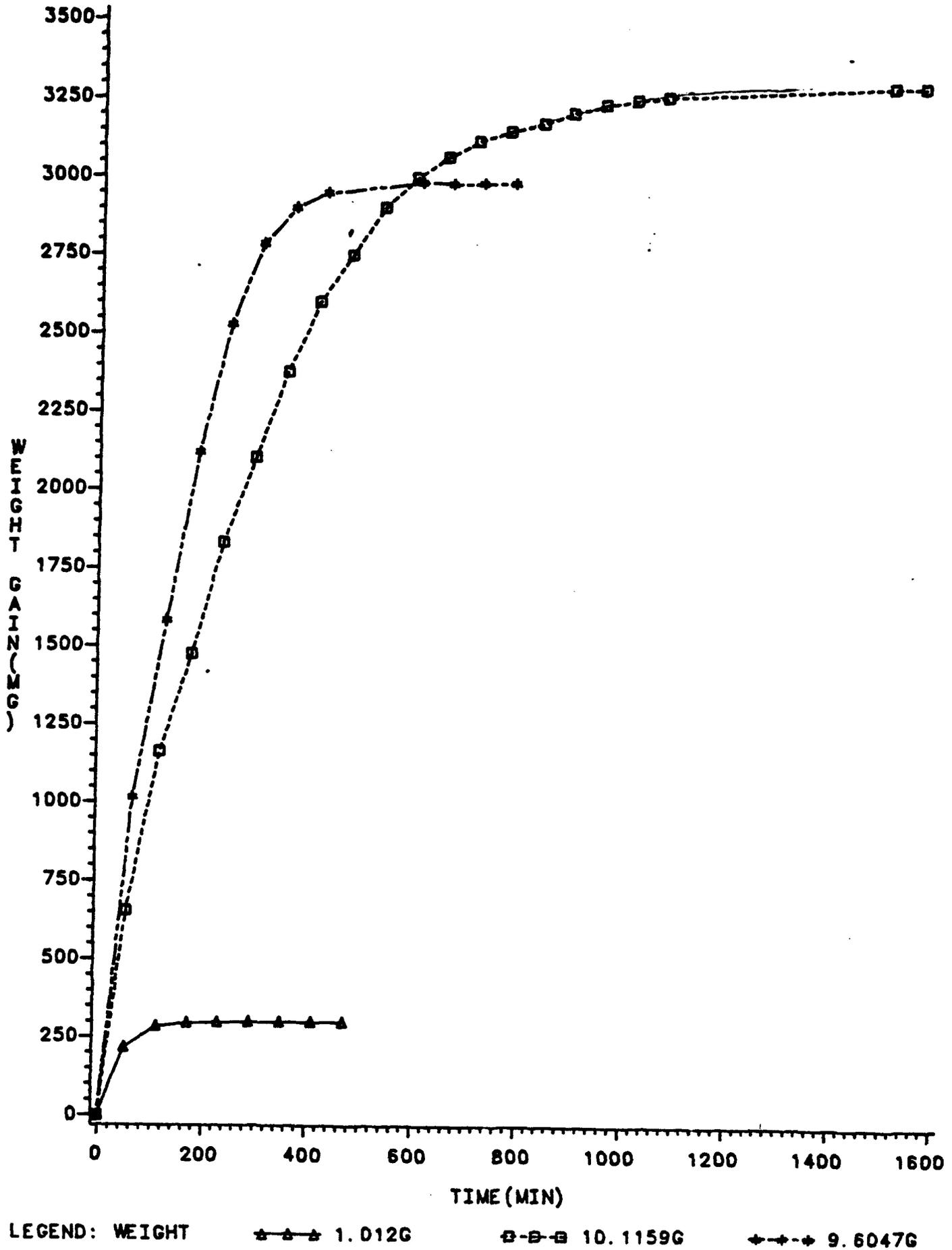
TABLE XXII

SUMMARY OF CONDITIONING DATA FOR ASC WHETLERITE

Sample Size (g)	Bed Height (cm)	Bed Diameter (cm)	Flow Rate (L/min)	Linear Flow Rate (cm/sec)	Contact Time (sec)	Kinetic Time (min)	Saturation Capacity (mg/g)
1.0120	0.6	2.3	1.0	0.25	0.15	350	299
9.6047	2.5	3.5	2.0	0.29	0.72	500	310
10.1159	2.5	3.0	1.0	0.42	1.06	1300	325

HUMIDITY CONDITIONING OF ASC WHETLERITE
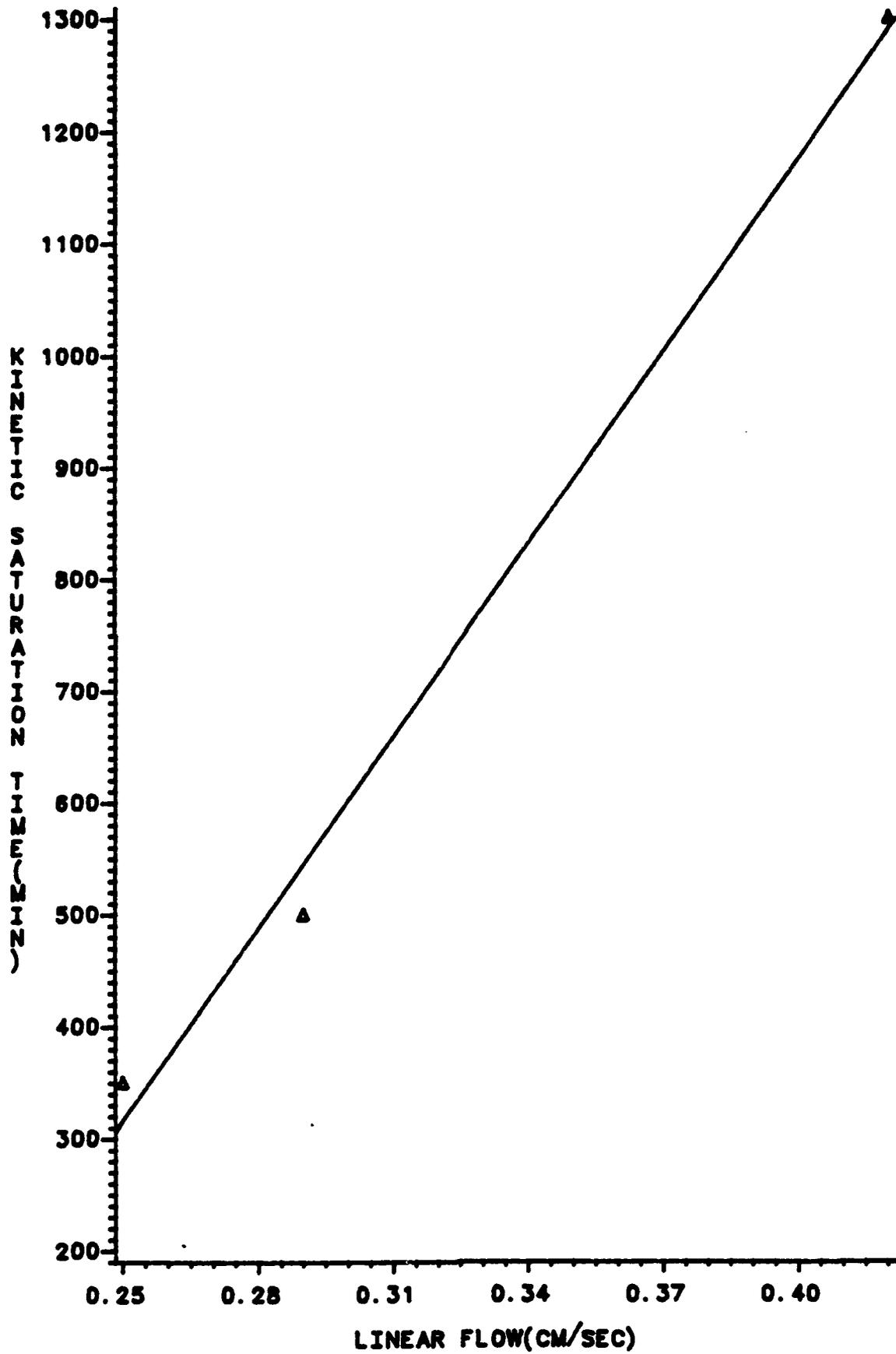
In accordance with Figures 18 and 19, adsorbent samples were preconditioned for BDST evaluation in ten gram lots at a flow rate of 1 1/min for a period of 24 hours. These samples were then challenged with DFP adsorbate in 95% RH air streams.

The DFP stream was formed by passing the humid nitrogen stream over the surface of DFP contained in a bubbler and bubbled into an impinger for calibration of the stream with respect to DFP content. Since there was concern about hydrolysis of the DFP in the bubbler and in the vapor stream, the calibration was performed in two ways.

In the first method, the humid DFP stream was bubbled into the first of three impingers connected in series, each containing 15 mL of 0.01N sodium isobutyrate buffer (pH of 5.5). In this buffer solution, the half life of DFP would be slightly less than 113 hours (85-87) and when analyzed using a calibrated fluoride specific electrode, only fluoride due to HF produced in a hydrolysis reaction in the bubbler on stream would be detected. The DFP present in the impinger would then be hydrolyzed by the addition of 0.1N NaOH, allowed to stand for 15 minutes and then analyzed for fluoride again. The increase in fluoride ion concentration would then be due to the DFP present in solution and could be related to the DFP concentration in the stream through the time and rate of flow. If all of the DFP was not collected in the first impinger, then significant fluoride ion concentrations would be seen in the second and third impingers of the series after hydrolysis. In each calibration, no significant fluoride was detected in the samples prior to hydrolysis. This indicated little HF was being formed in the stream from vapor phase hydrolysis or from hydrolysis in the bubbler. Also, the fluoride levels in the second and third impingers were determined to be negligible. Since no hydrolysis of DFP was detected, a second method was used in which the challenge stream was bubbled directly into a 4% caustic solution where it was hydrolyzed immediately.

The representative calibration data for the fluoride electrode in the sodium isobutyrate is tabulated in Table XXIII and plotted in Figure 20. As shown in Figure 20, the plot of ln]F-] vs mV is very linear over the concentration range studied with an intercept of -7.69, a slope of -0.0400, and a correlation coefficient of -0.9995.

TABLE XXIII

CALIBRATION DATA FOR THE FLUORIDE ELECTRODE

$[F^-]$ M	$\ln[F^-]$	Electrode Response mV
1×10^{-2}	-4.60	-76.8
1×10^{-3}	-6.91	-17.5
1×10^{-4}	-9.21	+39.2
5×10^{-5}	-11.5	+83.9
1×10^{-6}	-13.8	+105.5

FIGURE 20

CALIBRATION CURVE FOR THE FLUORIDE ELECTRODE
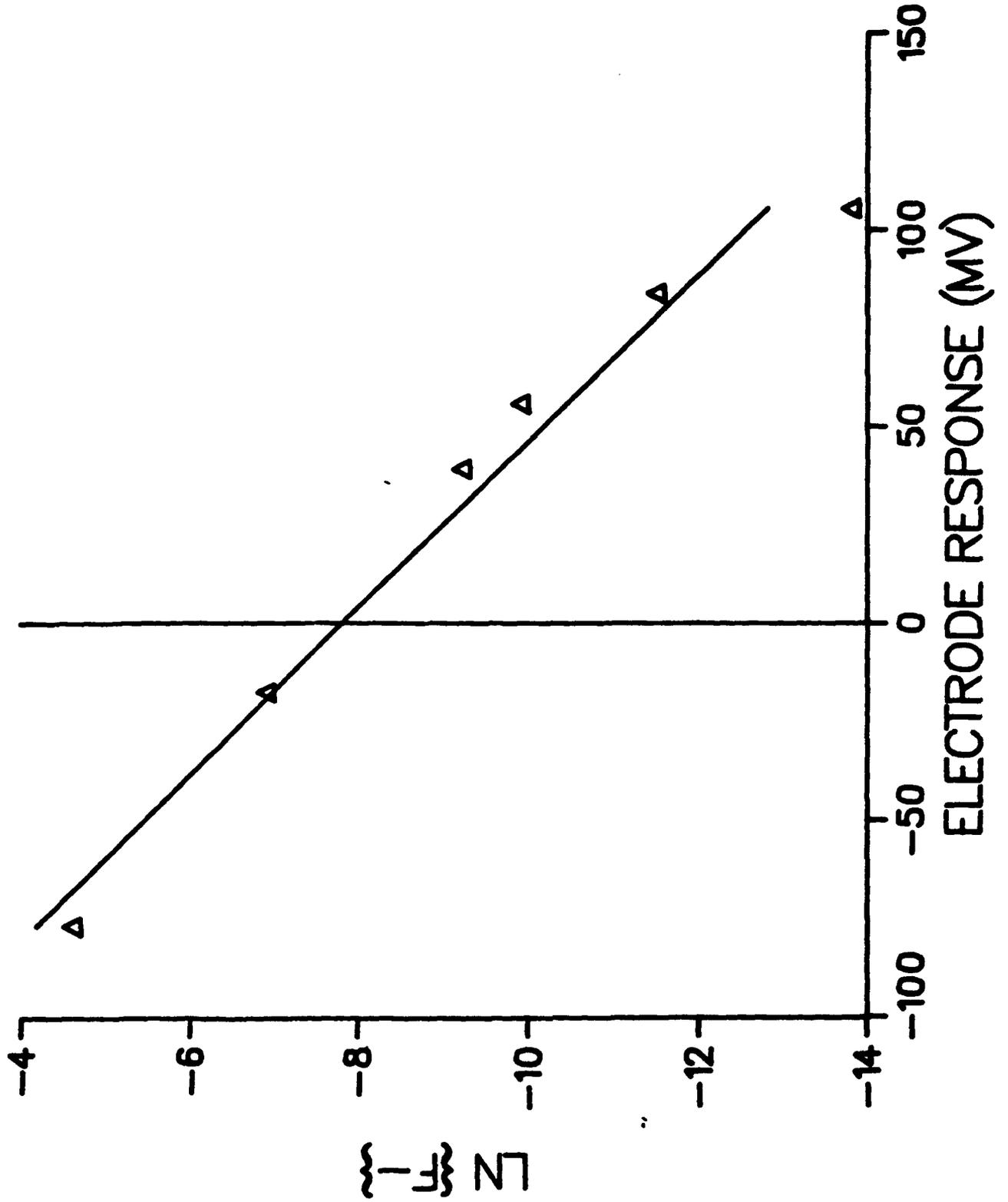
Table XXIV shows the results of our evaluation of the effects of conditioning and of high humidity on the ability of ASC Whetlerite to adsorb DFP from air streams. These data are plotted in Figure 21 and the results of the BDST treatment of the data are listed in Table XXV. These data show that ASC Whetlerite that has been humidified to 97% RH for 24 hours, and then challenged with a dry DFP stream shows an increase in the critical bed depth, but does not show a loss in the kinetic saturation capacity. However, when the ASC Whetlerite was conditioned for 24 hours at 97% RH and then challenged with a 97% RH DFP stream, a 90% decrease in the kinetic saturation capacity was noted. The poor correlation coefficient has been noted previously for carbon challenged under highly humid conditions (59).

TABLE XXIV - RESULTS OBTAINED WITH ASC WHETLERITE WITH DFP CHALLENGE UNDER HUMID CONDITIONS

Conditioning	Sorbent Weight (g)	Bed Height (mm)	RH of DFP Stream (%)	Concentration DFP Stream (mg/L)	Break Time (min)	Break Capacity (mg/g)	P
24 hrs 97% RH	1.9022	38	~95	1.76	16	15	0.50
24 hrs 97% RH	2.3871	51	~95	1.76	21	16	
24 hrs 97% RH	3.6164	76	~95	1.76	51	25	
Ambient RH	1.4492	25	0	2.27	144	225	
Ambient RH	2.9623	51	0	1.90	362	232	
Ambient RH		76	0				
24 hrs 97% RH	2.3672	38	0	1.90	136	109	
24 hrs 95% RH	3.2252	52	0	1.83	289	164	
24 hrs 97% RH	4.5312	76	0	2.10	399	184	
Dry	1.2740	25	0	1.92	120	181	
Dry	2.5192	51	0	2.02	304	244	
Dry	3.7901	76	0	2.04	487	262	

DFP BDST PLOT FOR ASC WHETLERITE UNDER DRY AND HUMID CONDITIONS
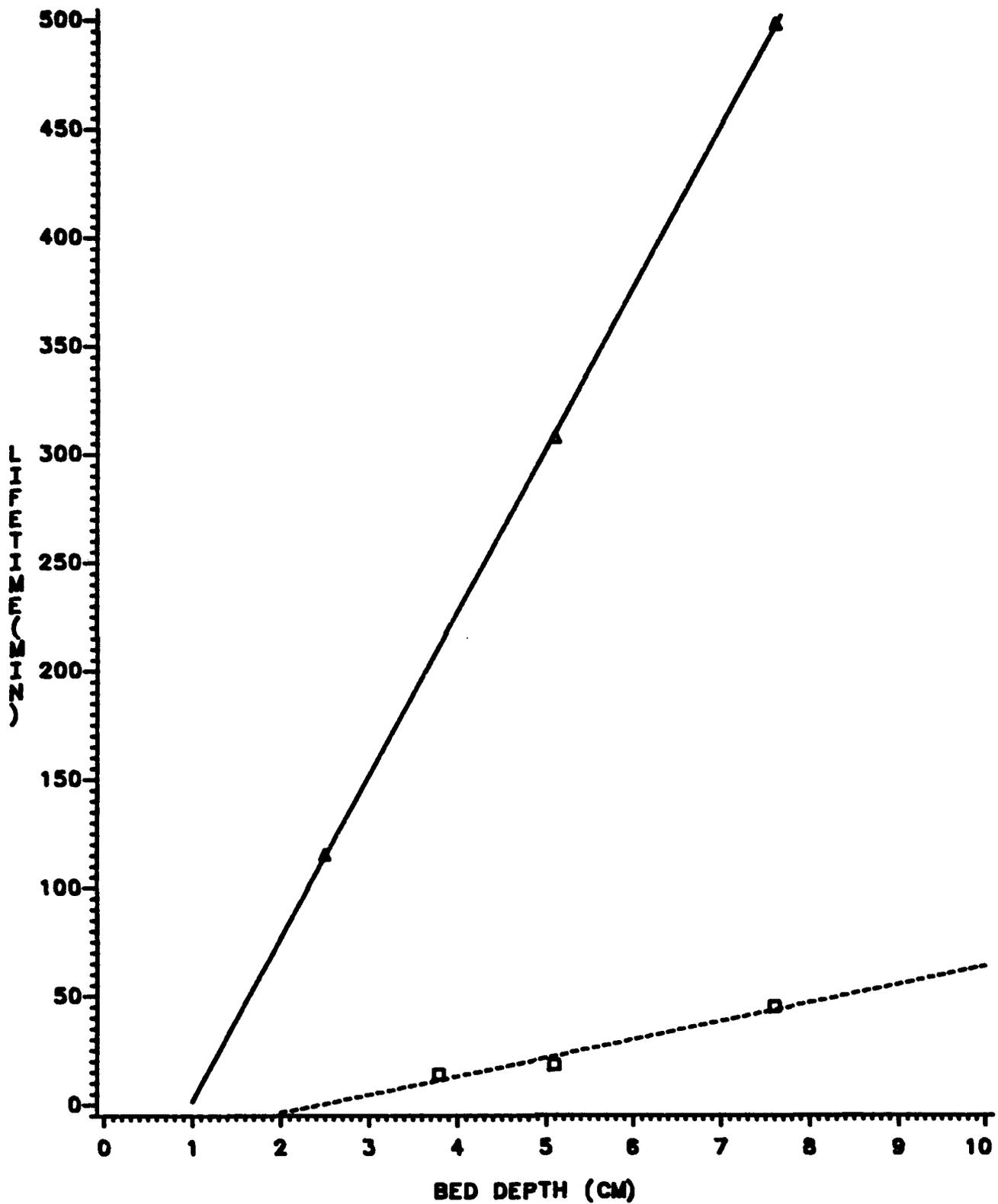
TABLE XXV - RESULTS OF BDST TREATMENT OF ASC WHETLERITE
UNDER VARIOUS HUMIDITY CONDITIONS

Conditioning	RH of Stream %	Regression Equation $tb=aDo+b$	Correlation Coefficient	Critical Bed Depth (cm)	Rate of Adsorption Front, S (cm/min)	Kinetic Saturation Capacity (mg/g)
24 hr 97% RH	~95	8.43Do-20.6	0.9779	2.6	0.1186	37.9
Ambient	0	82.3Do-5.5	0.9959	0.7	0.0122	369
24 hr 97% RH	0	75.0Do-144	0.9938	2.0	0.01333	337
Dry	0	74.9Do-73.1	2.000	1.0	0.0234	336

TABLE XXVI - POLYMERIC ADSORBENTS RUN UNDER HUMID CONDITIONS

Adsorbent	Conditioning	Sorbent Weight (g)	Bed Height (mm)	RH of DFP Stream (%)	Concentration DFP Stream (mg/L)	Break Time (min)	Break Capacity (mg/g)
P-2	24 hr 97% RH	0.7440	38	~95	1.94	123	321
		1.4858	76	~95	1.90	325	437
P-10	24 hr 97% RH	0.8401	38	~95	1.69	130	261
		1.1472	52	~95	1.94	210	355
		1.8071	76	~95	1.05	572	352
P-11	24 hr 97% RH	0.7641	38	~95	1.38	247	446
		1.0554	52	~95	1.96	233	433
		1.5932	76	~95	1.31	479	394
P-12	24 hr 97% RH	0.8930	38	~95	1.68	211	396
		1.1663	52	~95	1.34	351	406
		1.7256	76	~95	2.32	330	444
N-8	24 hr 97% RH	1.3755	38	~95	0.84	547	334
		2.7902	76	~95	0.96	2200	758

Table XXVI shows the results we have obtained with polymeric adsorbents under high humidity. The results of the BDST treatment are plotted in Figures 22 thru 26 and are summarized in Table XXVII. Table XXVII also compares the results obtained under high humidity with the results that we have obtained with low humidity.

The data in Table XXVII shows that high humidity has a much smaller effect on the ability of the synthetic adsorbents to adsorb DFP from humid streams than the effect of humidity on ASC Whetlerite. These adsorbents were preconditioned with a 95% air stream for approximately 20 hours prior to challenging with the humid DFP stream. The synthetic polymeric adsorbents showed only a small loss of capacity in the highly humid challenge experiments compared to that of ASC Whetlerite. The adsorbents P-10, P-11, showed a 14%, and a 36% loss of kinetic saturation capacity re pectively when compared to their ambient capacities. The synthetic adsorbent P-12, showed a 124% gain in kinetic saturation capacity when compared to that of its ambient capacity. This is certainly due to a low value of the ambient capacity as discussed previously in the low humidity testing section. The data for the adsorbents P-2 and N-8 are not complete since they only contain two points for each adsorbent. However, these data suggest that there is a minimal effect of humidity on the DFP adsorption capacity of these adsorbents. For the significance of this data to be appreciated fully, it must be compared to the data obtained with ASC Whetlerite which showed a 90% loss of kinetic saturation capacity when run under the highly humid conditions.

# DFP BDST PLOT FOR P–2 UNDER DRY AND HUMID CONDITIONS
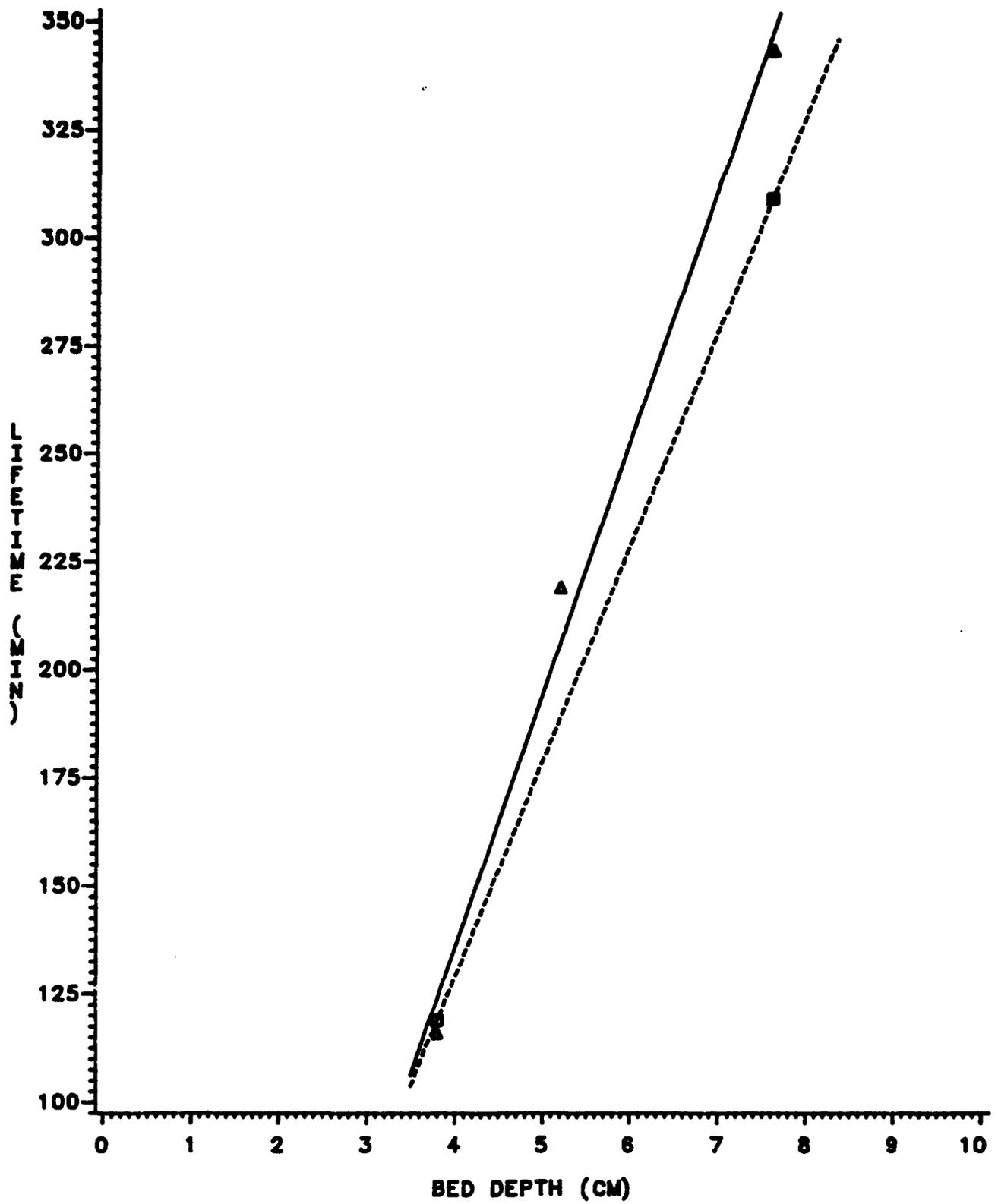
FIGURE 23.

# DFP BDST PLOT FOR P-10 UNDER DRY AND HUMID CONDITIONS.
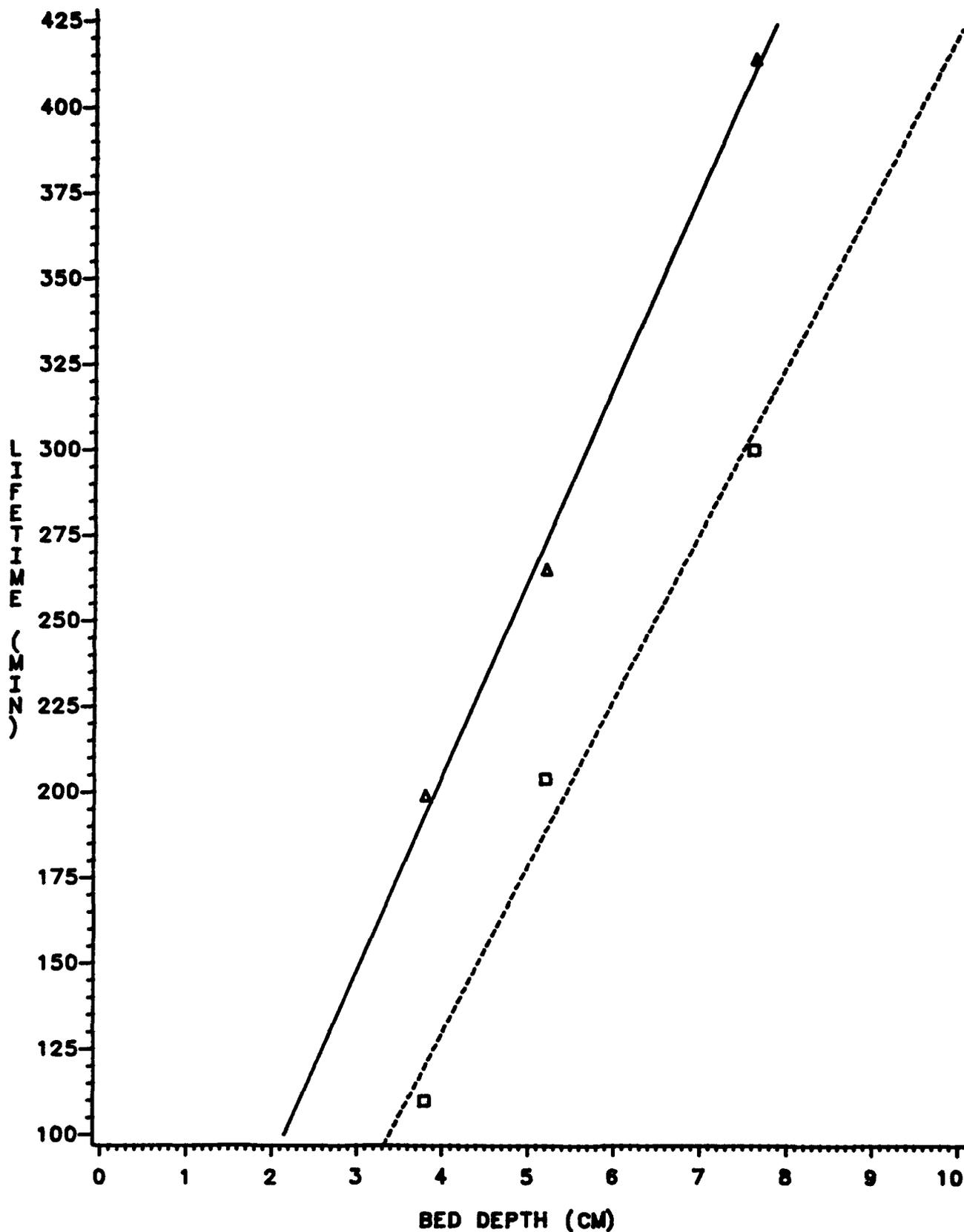
LEGEND: BED   ▲-▲-▲ DRY   ▣-▣-▣ HUMID

DFP BDST PLOT FOR P-11 UNDER DRY AND HUMID CONDITIONS

LEGEND: BED   △—△—△ DRY   ▣—▣—▣ HUMID
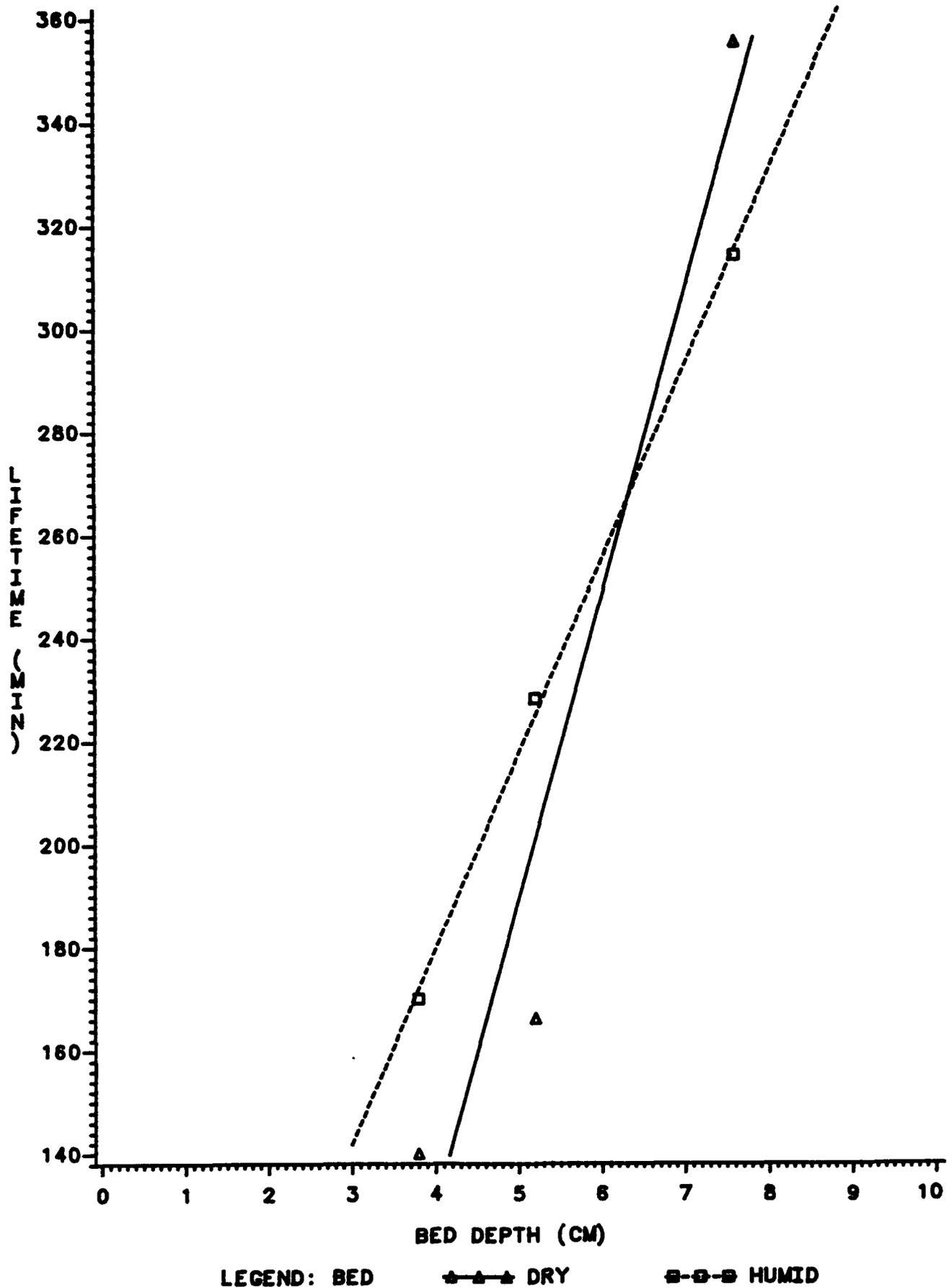
DFP BDST PLOT FOR P=12 UNDER DRY AND HUMID CONDITIONS

LEGEND: BED   ▲–▲–▲ DRY   ▣–▣–▣ HUMID
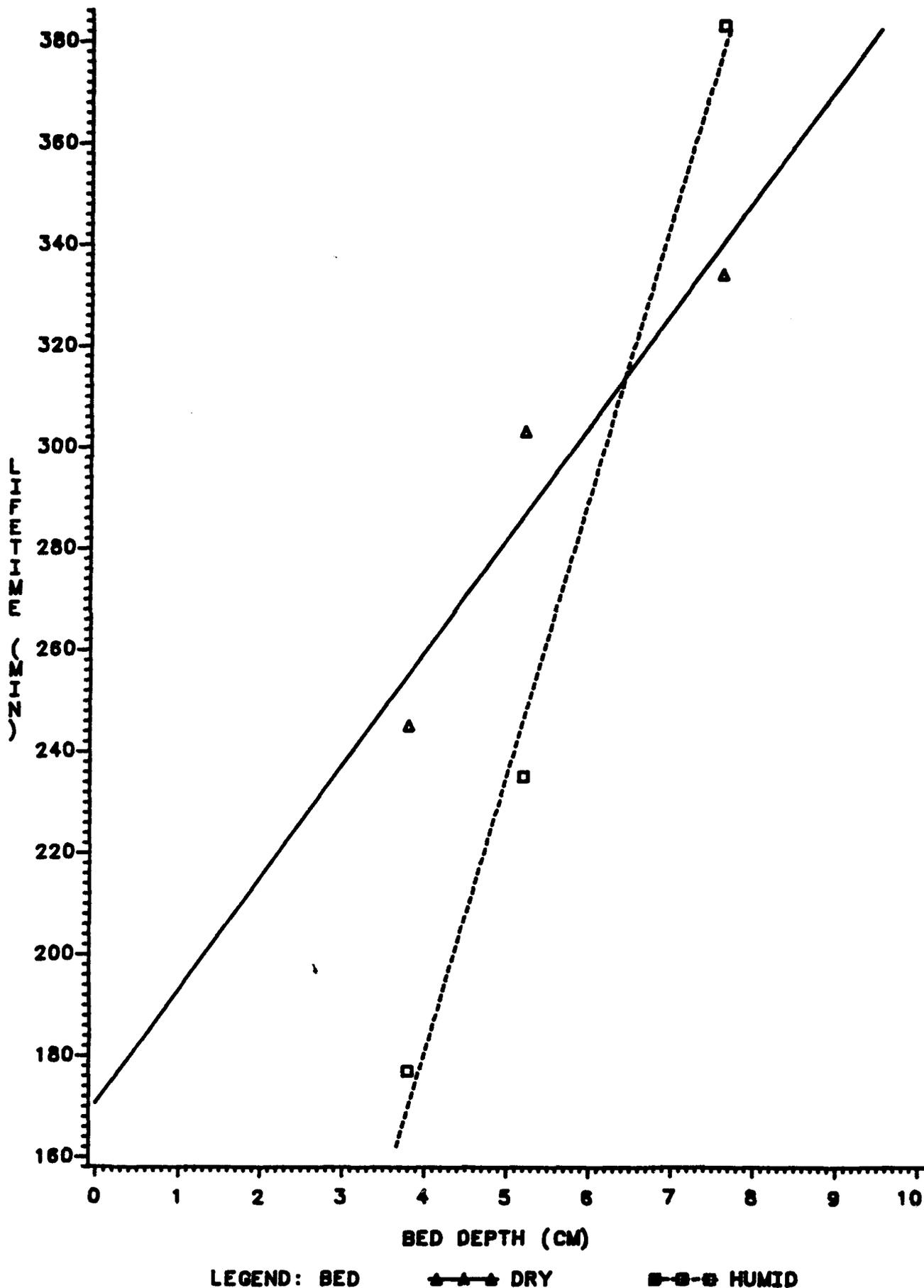
DFP BDST PLOT FOR N-8 UNDER DRY AND HUMID CONDITIONS

LEGEND: BED   ▲—▲—▲ DRY   ▣—▣—▣ HUMID
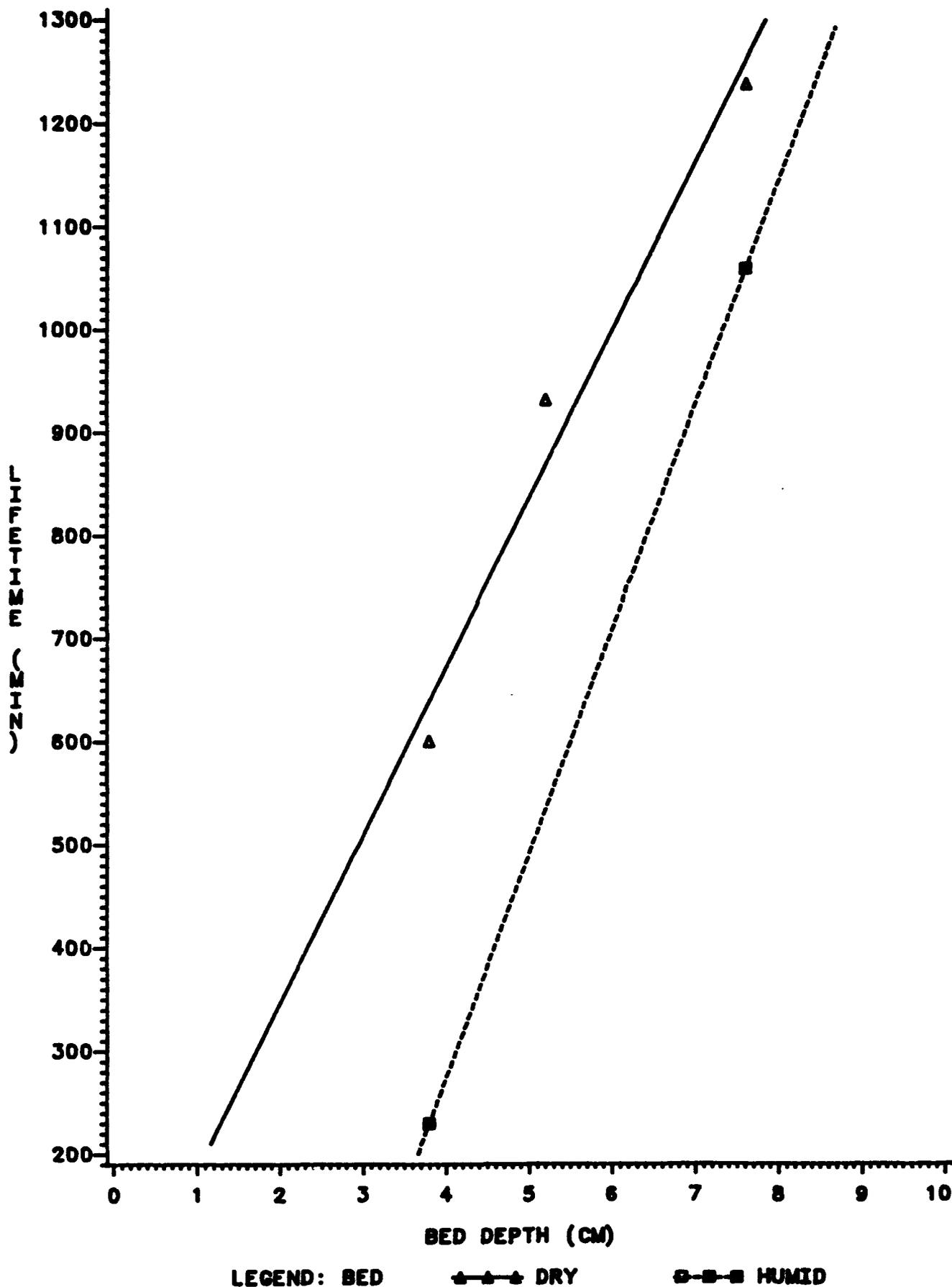
TABLE XXVII - RESULTS OF BDST TREATMENT OF POLYMERIC ADSORBENTS UNDER VARIOUS HUMIDITY CONDITIONS

Adsorbent	Conditioning	RH of Stream (%)	Regression Equation tb=aDo+b	Correlation Coefficient	Critical Bed Depth (cm)	Rate of Adsorption Front (cm/min)	Kinetic Saturation Capacity (mg/g)
P-2		0	58.9Do-99.7	0.9953	1.7	0.0170	667
P-2*	24 hr 97% RH	~95	50.0Do-71.0	1.000	1.4	0.0200	557
P-10		0	57.2Do-23.7	0.9977	0.4	0.0175	574
P-10	24 hr 97% RH	~95	48.9Do-66.0	0.9895	1.4	0.0204	493
P-11		0	59.0Do-106	0.9659	1.8	0.0169	656
P-11	24 hr 97% RH	~95	37.7Do-28.8	0.9992	-0.8	0.0265	419
P-12		0	22.3Do-171	0.9479	-6.4	0.0448	220
P-12	24 hr 97% RH	~95	48.9Do-66.0	0.9895	1.4	0.0204	493
N-8		0	163Do+29.4	0.9848	0.04	0.0061	1090
N-8*	24 hr 97% RH	~95	217Do-596	1.000	2.7	0.00460	1444

* Data for on 2 points

V.   CONCLUSIONS AND RECOMMENDATIONS

This contract has completed the screening studies on the synthetic polymeric macroporous and macronet adsorbents. These screening studies consisted of dynamic capacity measurements with DFP, CIS, and DMMP under dry conditions and hardness determinations. All adsorbents screened were of a particle size that had an identical pressure drop as that of ASC Whetlerite. The goal of the studies was to determine which samples warranted further and more detailed consideration in the program. The adsorbents with the lowest dynamic capacities and that were most susceptible to attrition were not considered for further studies.

Four polymeric macroporous adsorbents and one polymeric macronet adsorbent were studied further using the BDST technique. ASC Whetlerite was evaluated as a control for comparison. This technique measures breakthrough times as a function of bed height. In addition, a more varied series of challenges were used so that correlations could be developed with the volatility of the adsorbate. The adsorbents were challenged with methylene chloride, toluene, o-xylene, DMMP, DFP, and CIS under dry conditions. The synthetic adsorbents used in this study were not conditioned in any way prior to their evaluation. The ASC Whetlerite, however, was dried at 120°C and stored under vacuum prior to use.

Under conditions of low humidity, the BDST evaluation of the synthetic adsorbents and ASC Whetlerite showed a linear correlation with the boiling point of the adsorbent. The slope of the plot of kinetic saturation capacity vs boiling point of the adsorbate was greater for the synthetic adsorbents than it was for ASC Whetlerite. This indicates that the synthetic adsorbents have a lower kinetic saturation weight capacities for volatile adsorbates than ASC Whetlerite has, but higher kinetic saturation weight capacities for nonvolatile adsorbates such as DFP, CIS, and DMMP than ASC Whetlerite. Since the synthetic adsorbents have lower densities than ASC Whetlerite, the kinetic saturation volume capacities are comparable to that obtained with ASC Whetlerite under dry conditions.

The BDST technique was also used to evaluate adsorbents under conditions of high relative humidity with DFP. The synthetic adsorbents were conditioned for 24 hours under a 95% RH air stream prior to testing. The results show that when the conditioned adsorbents were challenged with a DFP stream at 95%, the adsorbents retained a large portion (up to 90%) of their dry kinetic saturation capacities.

ASC Whetlerite was also challenged with DFP under highly humid conditions. When the Whetlerite was conditioned under 95% RH for 24 hours prior to use, the BDST evaluation with DFP showed a loss of 90% of the kinetic saturation capacity of the carbon to adsorb the DFP from the challenge stream. However, further work showed that the ability of ASC Whetlerite to adsorb DFP was dependent on the method of the conditioning of the carbon.

We recommend that:

1. In addition to the adsorbents that were carried past screening, adsorbents designated P-6 and P-7 which show unusually high capacities with respect to their pore volume, should be evaluated using the BDST technique to better define the potential of these adsorbents. These adsorbents should be prepared as 200g blends of different preparations to eliminate batch to batch variations and to assure that the preliminary results are not characteristic of a particular preparation.

2. Since a major concern with adsorbents is that of desorption, evaluations of the desorption characteristics of the synthetic adsorbents should be determined. These studies should provide evidence as to how strongly the synthetic adsorbents hold on to the adsorbate which will permit the assessment of the risk of self contamination due to the mass transfer zone moving through the bed.

3. Further characterization of the synthetic polymeric adsorbents using helium pycnometry, low pressure mercury penetrometry, and nitrogen desorption porosimetry. In order to understand the behavior of the synthetic adsorbents, additional adsorbents need to be characterized thoroughly, and additional adsorbents need to be evaluated using the BDST technique. This will help in relating dynamic adsorption performance of the polymeric adsorbents to pore size, pore size distribution, and surface area.

4. The synthetic adsorbents need to be tested with actual live agents. All of the simulant testing that has been completed present a very positive case for the capability of the polymeric adsorbents, particularly at high relative humidities. However, the practical issues of how well these adsorbents perform can only be answered using live agents under realistic conditions.

5. The polymeric adsorbents should be evaluated under conditions where competitive adsorption take place. The shipboard environment that a filter would be exposed to on board a ship is not a clean one with respect to atmospheric pollutants (88). Results reported here indicate that polymeric adsorbents may be more selective than ASC Whetlerite with respect to volatile pollutants that may be present around a ship during routine operations or during combat situations. The effect of selected vapors on the performance of these adsorbents and ASC Whetlerite at high and low humidity with respect to capacity, ability to displace simulants, and regenerability should be investigated.

6. Chase Studies with simulants should be carried out to determine if one simulant is capable of displacing another simulant that is adsorbed on the adsorbent bed. A scenario that one can imagine is an attack by one or more agents followed by a second attack by one or more different agents. The agents that are more strongly adsorbed may displace more weakly held molecules and push them through the bed. Theoretically, this would provide a mechanism for defeating a filter system and could be considered a form of a "mask breaker". Chase studies with simulants as well as "mask breaker" studies should be carried out with the synthetic adsorbents and ASC Whetlerite to determine their scope and limitations under both dry and humid conditions. It would be prudent to consider similar studies with actual agent to determine how closely the simulants resemble agent under these conditions.

7. Development of a regenerable adsorbent for collective filters would relieve the uncertainties of residual bed life of fixed bed adsorbers and relieve logistical burdens associated with filter bed replacement. The ultimate goal of the project is to develop an adsorbent system that can be used as a filter medium in continuous use CB collective filters. Since all adsorbents have a finite capacity, either stores of medium must be maintained or the medium must be regenerable. We feel regenerability of adsorbent is preferable to replacement from both an economic and a logistic point of view. The regenerability of the adsorbents under consideration should be investigated to determine the scope and limits of their use as well as to gain an understanding of their use. Procedures that will be most compatible with the facilities and space requirements aboard a ship will be emphasized.

8. The synthetic adsorbents should be evaluated to see if weathering of the adsorbent causes a decrease in the ability of the adsorbent to remove organic vapors from flowing air streams. A problem with the ASC Whetlerite that is presently being used by the military is that of atmospheric weathering. Adsorbent media should be prepared and exposed to realistic weather conditions to determine if the adsorbents performance degrade with time.

9. Synthetic polymeric adsorbent should be placed in a filter canister and the performance of the resulting canister should be evaluated. The only way to actually evaluate the performance of a new medium is to build a prototype filter and to test it. We will supply NRL enough adsorbent to place in a canister of the type placed on ships so that shock testing, pressure drop measurements, and agent capacity can be studied.

10. The synthetic adsorbents should be optimized to minimize any deficiencies that are detected in the above studies. The studies mentioned above evaluate the performance of these media and should point out where deficiencies exist. Since these adsorbents are synthetic, modifications in the preparation of the adsorbents will minimize any detected deficiencies and optimize performance. Through modifications in the synthetic procedures, surface area, pore size distribution, functionality, degree of functionality, and hardness can be modified to improve the adsorbents performance of a synthetic adsorbent.

11. The synthetic adsorbent of choice should be scaled up and the synthetic procedure optimized with respect to yield, particle size, and reaction time. Under the present contract, large particle size adsorbents are prepared by making large particle size adsorbents and screening out the mesh cut that is desirable. The remaining beads are not useful for our purposes and are discarded. On a commercial scale, this is an inefficient method to produce a product. Optimization of the synthetic process will be a necessary requirement prior to commercialization of the process and the production of a viable adsorbent medium. Rohm and Haas plans to initiate scale up activities at its own expense in the near future. This program will not be dependent upon Government funding.

12. The toxicology that is associated with putting a new adsorbent in an air purification system should be pursued. In order to place new media in an air filtration system, it may be necessary to obtain certification from the Surgeon General. Initially, we will draw upon toxicology data that we have obtained on other Government projects to estimate the potential toxicological risks. Eventually, acute toxicology studies of the sorbents will be carried out. We will also characterize the vapors that may be given off under conditions of use before, during, and after a CB attack. These toxicology studies could be done by the Toxicology Department of the Rohm and Haas Company.

Bibliography

1. B. Chapman, "Navy CW Defense," National Defense, April, 1983, pp54-57.

2. N.W. Blaylock; E.P. Bergmann, "Engineering Assessment of Filter Technology. Final Report," Report Number AD B058449, June 1981.

3. N.W. Blaylock; R.G. Thresher, "NBC Filters at Government Installations," Report Number AD B067418, July 1982, p15.

4. E. Haupt, "DSK. NBC Protection in the German Navy," National Defense, April 1983, pp54-57.

5. L.A. Jonas; E.B. Sansome; T.S. Farris, Am. Ind. Hyg. Assoc. J., 1985, 46(1),

6. G.O. Nelson; A.N. Corrcia; C.A. Harder, Am. Ind. Hyg. Assoc. J., 1976, 37, 280-288.

7. I.V. Potorzhinskii; E.N. Serpionova, Tr. Mosk. Khim.-Tekhnol. Inst., 1970, 65, 79-82.

8. J.R. Conlisk; S.L. Carr, "Effect of Humidity and Gas Concentration on the Adsorption of GB and PS by Micronized ASC Charcoal," Report Number AD 97099, 31 January, 1956.

9. R.S. Braman; J. Pritchard; W.J. Wheeler, "Preparation and Evaluation of Noncarbonaceous Sorbents," Report Number AD 833258, April, 1968.

10. R.H. van Dongen; P.C. Stamperious, "The Dynamics of Adsorption of Vapours by Porous Adsorbents in Fixed Beds," Report Number AD B002363, 1974.

11. J.O. Smith; B.M. Fabuss; D.A. Duncan; C.H. Lu, "New Concept Studies, CW Defense," Report Number AD 455358, 15 August 1964.

12. T. Fouyn; B.H. Harrison, "Performance of Charcoal Filters I. Effect of Relative Humidity," Report Number AD C028984 (DREO-R857), February 1982.

13. B.H. Harrison; R. Poirier; T. Fouyn, "The Performance of Charcoal Filters II. Chloropicrin: The Effect of Relative Humidity," Report Number AD C029151 (DREO-R860), March 1982.

14. W.F. Kladnig; A.H. Weiss; L.A. Jonas, Carbon, 1980, 18, 31-35.

15. J. Medema; J.J.G.M. v Bokoven," Nondestructive Test Methods," Report Number AD B063334, October 1980.

16. N. Bac; A. Sacco; J. Hammarstrom," Residual Life Method for Determining Gas Protection of ASC Whetlerite Carbon Beds, Quarterly Progress Report Number 4, July 1981 - September 1981," Report Number AD B067640, June 1982.

17. M.M Dubinin; V.V. Serpinskii, Dokl. Akad. Nauk. SSSR, 1954, 99, 1033-

18. M.M Dubinin, Igv. Akad. Nauk., SSSR, Ser. Khim., 1981, 9-

19. G.A. Andreeva; N.S. Polyakov; M.M. Dubinin; K.M. Nikolaev. B. Acad. Sci. USSR, 1981, 30(10), 1795-1799.

20. G.A. Andreeva; N.S. Polyakov; M.M. Dubinin; K.M. Nikolaev; E.A. Ustinov, B. Acad. Sci. USSR, 1981, 30(19), 1791-1795.

21. M.M Dubinin; K.M. Nikolaev; N.S. Polyakov; G.L. Pirozhkov; N.V. Filimonov, Bull. Acad. Sci., 1982, 31(11), 2137-2141.

22. N.I. Petrova; K.M. Nikolaev, J. Appl. Chem. USSR, 1984, 11, 2131-2134.

23. M.M. Dubinin; G.A. Andreeva; R. Sh. Vartapetyan; S.P. Vnukov; K.M. Nikovaev; N.S. Polyakov; N.I. Seregina; D.V. Fedoseev, Bull. Acad. Sci., 1982, 31(11), 2133-2137.

24. N.W. Blaylock; E.P. Bergmann," Engineering Assessment of Filter Technology, Final Report," Report Number AD B048449, June 1981.

25. A.H. Weiss; R. Szostak," Zeolite Catalyst for Gas Mask Canisters," Report Number B078296, June, 1983.

26. S.G. Maroldo, "Development of a Synthetic, Humidity Resistant, High Capacity Adsorbent for Collective Air Filters for Naval Vessels. Phase I." Final Report for Contact Number N000-82-C-2383, 7 May 1984.

27. "Summary Bulletin Amberlite Polymeric Adsorbents," Rohm and Haas Company Bulletin IE-172, September, 1981.

28. Ig. C. Poinescu; C. Beldie; C. Vlad, J. Appl. Polymer Science, 1984, 29, 23-34.

29. J. Lieto; D. Milstein; R.L. Albright; J.V. Minkiewicz; B.C. Gates, Chemtech, 1983, January, 46-53.

30. E.F. Meitzner; J.A. Oline, U.S. Patent 4,297,220, 27 October, 1981.

31. W. Heitz in "Advances in Polymer Science," H.J. Cantow, Ed. Springer-Verlog, Nre York 1977.

32. R.L. Albright, U.S. Patent 3,767,600, 1973.

33. R.L. Albright, U.S. Patent 3,663,467, 1972.

34. K.A. Kun; R.J. Kunin, J. Polym. Sci. A-1, 1968, 6, 2689-2701.

35. K.A. Kun; R.J. Kunin, J. Polym. Sci. C-16, 1967, 1457-1469.

36. I.C. Poinescu; C. Beldie; C.Vlad, J. Appl. Poly. Sci., 1984, 29, 23-34.

37. D.C. Sherrington, British Polymer J., 1984, 16(4), 164-172.

38. R.S. Mikhail; E. Robens, "Microstructure and Thermal Analysis of Solid Surfaces," Wiley Heyden Ltd., New York, 1983, p 159.

39. G.I. Rosenburg; A.S. Shabaeva; V.S. Moryakov; T.G. Musin; M.P. Tsyurupa; V.A. Davankov, Reactive Polymers, 1983, 1, 175-182.

40. S.F. Reed, Jr., U.S. Patent 4,263,407, "Polymeric Adsorbents from Macroreticular Polymer Beads, 21 April, 1981.

41. R.K. Pinschmidt; S.F. Reed, U.S. Patent 4,191,813, "Polymeric Adsorbents from Vinylbenzene Chloride Copolymer Beads, Ion Exchange Resins Crosslinked by a Lewis Acid,"

42. V.A. Davankov; M.P. Tsyurupa, Angew. Makro., 1980, 91, 127-142.

43. M.P. Tsyurupa; V.A. Davankov, J. Poly Sci:Poly Chem. Ed., 1980, 18, 1399-1406.

44. M. Negre; M. Bartholin; A. Guyot, Angew. Makro., 1979, 80, 19-30.

45. M.P. Tsyurupa; A.I. Andreeva; V.A. Davankov, Angew. Makro., 1978, 70, 179-187.

46. A.I. Subbotin; N.G. Sukhikh, J. Appl. Chem., 1982, 55(1), 53-57.

47. R.C. Weast, ed. "Handbook of Chemistry and Physics," 54th Edition, CRC Press, Cleveland, Ohio, 1973, p E-46.

48. R.C. Weast, ed. "Handbook of Chemistry and Physics," 54th Edition, CRC Press, Cleveland, Ohio, 1973, p D-230.

49. R.C. Weast, ed. "Handbook of Chemistry and Physics," 54th Edition, CRC Press, Cleveland, Ohio, 1973, p F-103.

50. G.B. Freeman; P.J. Reucroft, Carbon, 1979, 17, 313-316.

51. M.M. Dubinin; E.D. Zaverina; L.V. Radushkevich, Zh. Fiz. Khim., 1947, 21, 1351- .

52. C.T. Chiou; P.J. Reucroft, Carbon, 1977, 15, 49-53.

53. D.M. Ruthven, "Principles of Adsorption and Adsorption Processes," Wiley-Interscience, New York, 1984.

54. C.T. Chiou; P.J. Reucroft, Carbon, 1977, 15, 49-53.

55. M.M. Dubinin, Chem. Rev., 1060, 60, 235-241.

56. Anonymous, "Vaisala Humicap Humidity Meter Instruction Manual," VAISALA, oy, PL26 SF-00421, Helsink 42, Finland.

57. L.A. Jonas; W.J. Svirbely, J. Cat., 1972, 24, 446-459.

58. L.A. Jonas; J.A. Rehrmann, Carbon, 1972, 10, 657-663.

59. R.A. Hutchins, Chem. Eng., 1973, 80(3), 133-138.

60. L.A. Jonas; J.A. Rehrmann, Carbon, 1973, 11, 59-64.

61. A. Wheeler; A. Robell, J. Catal., 1969, 13, 299-305.

62. G.S. Bohart; E.Q. Adams, J. Amer. Chem. Soc., 1920, 42, 523-544.

63. I.M. Klotz, Chem. Rev., 1946, 39, 241-268.

64. M. Dole; I.M. Klotz, Ind. Eng. Chem. 1946, 38, 1289-1297.

65. B. Staginnus, "Adsorption of Cyanogen Chloride and Chloropicrin on Activated Carbon," Extended Abstracts and Program of the 15th Biennial Conference on Carbon, Philadelphia, 1981.

66. D.M. Ruthven, "Principles of Adsorption and Adsorption Processes," Wiley-Interscience, New York, NY, 1984, pp261-272.

67. D.O. Cooney; N. Lightfoot, Ind. Eng. Chem. Fund., 1965, 4, 233-

68. A.S. Michaels, Ind. Eng. Chem., 1952, 44, 1922-1930.

69. R.E. Treyball, "Mass Transfer Operations," 2nd Edition, McGraw Hill, 1968, pp550-556.

70. G.M. Lukchis, Chem. Eng., 1973, 80, 111-116.

71. N.K. Hiester; T. Vermeulen, Chem. Eng. Progr., 1952, 48, 506-

72. J.W. Neely; E.G. Isacoff, "Carbonaceous Adsorbents for the Treatment og Ground and Surface Waters," Marcel Dekker, Inc., New York, 1982, Chapter 3.

73. M. Windholz; S.Budavari; L.Y. Stroumtsos; M.N. Fertig, "The Merk Index," Mrek & Co. Inc., Rahway, NJ,1976.

74. R.C. Weast, "Handbook of Chemistry and Physics," 54th Edition, CRC Press, Cleveland, OH, 1973, pD162.

75. A.W. Adamson, "A Textbook of Physical Chemistry," Academic Press, New York, 1973, p 296.

76. S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Company. Inc., New York, 1946, p 1197.

77. G.O. Nelson; C.A. Harder; B.E. Bigler, "Respirator Cartridge Efficiency Studies: VI Effect of Concentration. Rept UCRL-76184. Lawrence Livermore Laboratory, 1974.

78. S.J. Gregg; K.S.W. Sing, "Adsorption, Surface Area and Porosity," Second Edition, Academic Press, New York, 1982, p 238.

79. P.H. Emmet, Chem. Rev., 1948, 43, 69-148.

80. M.M. Dubinin; V.V. Serpinskii, Dokl. Akad. Nauk. SSSR, 1954, 99, 1033-

81. M.M. Dubinin, Igv. Akad. Nauk. SSSR, Ser. Khim., 1981, 9-.

82. G.A. Andreeva; N.S. Polyakov; M.M. Dubinin; K.M. Nikolaev; E.A. Usinov, B. Acad. Sci. USSR, 1981, 30(10), 1791-1795.

83. G.A. Andreeva; N.S. Polyakov; M.M. Dubinin; K.M. Nikolaev; E.A. Usinov, B. Acad. Sci. USSR, 1981, 30(19), 1791-1795.

84. M.M Dubinin; K.M. Nikolaev; N.S. Polyakov; G.L. Pirozhkov; N.V. Filimonov, Bull. Acad. Sci., 1982, 31(11), 2137-2141.

85. W.A. Waters; C.G.M. deWorms, J. Chem. Soc., 1949, 926-

86. M. Kilpatrick, Jr.; M.L. Kilpatrick, J. Phys. Colloid. Chem., 1949, 53, 1371-

87. M. Kilpatric,Jr.; M.L. Kilpatrick, J. Phys. Colloid. Chem., 1949, 53, 1385-

88. R.A. Lamontagne; L. Isaacson, "Characterization of Shipboard Atmospheric Environments", NRL Memorandum Report Number 5537, 29 March 1985

89. S. Brunauer; L.S. Deming; W.E. Deming; E.J. Teller, J. Am. Chem. Soc., 62, 1723-   (1940).